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(51) Internationale Patentklassifikation [6] : C04B 35/573, 35/80, F16D 69/02	A1	(11) Internationale Veröffentlichungsnummer: **WO 98/42634** (43) Internationales Veröffentlichungsdatum: 1. Oktober 1998 (01.10.98)

(21) Internationales Aktenzeichen: PCT/EP98/00951

(22) Internationales Anmeldedatum: 19. Februar 1998 (19.02.98)

(30) Prioritätsdaten:
197 11 831.3   21. März 1997 (21.03.97)   DE

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(81) Bestimmungsstaaten: BR, BY, CA, CN, CZ, JP, KR, PL, RU, US, europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Veröffentlicht
Mit internationalem Recherchenbericht.

(54) Title: FIBRE–REINFORCED COMPOSITE CERAMICS INFILTRATED WITH MOLTEN METAL

(54) Bezeichnung: SCHMELZINFILTRIERTE FASERVERSTÄRKTE VERBUNDKERAMIK

(57) Abstract

The invention concerns fibre–reinforced composite ceramics infiltrated with molten metal and comprising high–temperature fibres, in particular based on Si/C/B/N, which are bound in terms of reaction to an Si–based matrix. The invention also concerns a method of producing such ceramics. The molten silicon used for infiltration purposes contains additions of iron, chromium, titanium, molybdenum, nickel or aluminium, molten silicon containing approximately 5 to 50 weight % iron and approximately 1 to 10 weight % chromium being particularly preferred. The production method is simpler than conventional molten silicon infiltration methods and imparts improved properties to the composite ceramics.

(57) Zusammenfassung

Es wird eine schmelzinfiltrierte, faserverstärkte Verbundkeramik mit hochwarmfesten Fasern, insbesondere auf der Basis von Si/C/B/N, die mit einer Matrix auf Si–Basis reaktionsgebunden sind, sowie ein Verfahren zur Herstellung einer solchen angegeben. Die Siliziumschmelze, die zur Schmelzinfiltrierung verwendet wird, enthält Zusätze von Eisen, Chrom, Titan, Molybdän, Nickel oder Aluminium, wobei eine Siliziumschmelze, die etwa 5 bis 50 Gew.–% Eisen und etwa 1 bis 10 Gew.–% Chrom enthält, besonders bevorzugt ist. Es ergeben sich ein vereinfachtes Herstellverfahren im Vergleich zu herkömmlicher Silizium–Schmelzinfiltrierung und verbesserte Eigenschaften der Verbundkeramik.

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(12) **Patent Application:**   (11) **CA 2284614**

(54) FIBRE, REINFORCED COMPOSITE CERAMICS INFILTRATED WITH MOLTEN METAL

(54) CERAMIQUE COMPOSITE RENFORCEE PAR FIBRES, INFILTREE AVEC UNE MATIERE FONDUE

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ABSTRACT:
The invention concerns fibre-reinforced composite ceramics infiltrated with molten metal and comprising high-temperature fibres, in particular based on Si/C/B/N, which are bound in terms of reaction to an Si-based matrix. The invention also concerns a method of producing such ceramics. The molten silicon used for infiltration purposes contains additions of iron, chromium, titanium, molybdenum, nickel or aluminium, molten silicon containing approximately 5 to 50 weight % iron and approximately 1 to 10 weight % chromium being particularly preferred. The production method is simpler than conventional molten silicon infiltration methods and imparts improved properties to the composite ceramics.

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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(45) Issued:

(86) PCT Filing Date: **Feb. 19, 1998**

(87) PCT Publication Date: **Oct. 1 , 1998**

Examination requested: **May 11, 2000**

(52) Canadian Class (CPC): **75/1.2**

(51) International Class (IPC): **F16D 69/02**
C04B 35/573
C04B 35/80

Patent Cooperation Treaty (PCT): **Yes**

(85) National Entry:	Sep. 21, 1999
(86) PCT Filing number:	PCT/EP1998/000951
(87) International publication number:	WO1998/042634

(30) Application priority data:

Application No.	Country	Date
197 11 831.3	Germany (Federal Republic of)	Mar. 21, 1997

Availability of licence: **N/A**

Language of filing: **English**

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Patent Document Number 2284614 :
FIBRE, REINFORCED COMPOSITE CERAMICS INFILTRATED WITH MOLTEN METAL

CERAMIQUE COMPOSITE RENFORCEE PAR FIBRES, INFILTREE AVEC UNE MATIERE FONDUE

CLAIMS:

Claims

1. Melt-infiltrated fibre-reinforced composite ceramic containing high-temperature-resistant fibres, in particular fibres based on Si/C/B/N, which are reaction-bonded to a matrix based on Si and containing at least one addition of another material, characterized in that the matrix contains additions of iron.

2. Composite ceramic according to Claim 1, characterized in that the matrix contains additions of chromium, titanium, aluminium, nickel or molybdenum as passive layer formers.

3. Composite ceramic according to any of the preceding claims, characterized in that the matrix is produced from a silicon alloy containing from 0.5 to 80% by weight of iron.

4. Composite ceramic according to Claim 3, characterized in that the matrix is produced from a silicon alloy containing from 5 to 50% by weight of iron.

5. Composite ceramic according to any of the preceding claims, characterized in that the matrix is produced from a silicon alloy containing from 0.03 to 40% by weight of chromium.

6. Composite ceramic according to any of the preceding claims, characterized in that the matrix is produced from a silicon alloy containing from 1 to 40% by weight of chromium.

7. Composite ceramic according to any of the preceding claims, characterized in that the matrix is produced from a silicon alloy containing from 1 to 10% by weight of chromium.

8. Composite ceramic according to any of the preceding claims, characterized in that the fibres are C fibres or SiC fibres.

9. Composite ceramic according to any of the preceding claims, characterized in that the fibres are collected together to form fibre bundles and are surface-impregnated.

10. Composite ceramic according to Claim 9, characterized in that the fibres are collected together to form short-fibre bundles.

11. Composite ceramic according to Claim 10, characterized in that the fibres comprise C filaments having mean diameters of from about 5 to 12 µm and a length of from about 2 to 10 mm which are collected together to form fibre bundles containing from about 3000 to 14,000 filaments.

12. Process for producing a fibre-reinforced composite ceramic containing high-temperature-resistant fibres, in particular fibres based on Si/C/H/N, which are reaction-bonded to a matrix based on Si, comprising the following steps:
- production of a green body from fibres using binders and fillers by winding, lamination or pressing;
- pyrolysis of the green body under reduced pressure or protective gas in a temperature range from about 800°C to 1200°C to produce a porous shaped body (14);
- infiltration of the porous shaped body (14) with a silicon melt which contains additions of iron.

13. Process according to Claim 12, in which the silicon melt contains additions of chromium, titanium, aluminium, nickel or molybdenum as passive, layer formers.

14. Process according to Claim 12 or 13, in which the silicon melt contains from 0.5 to 80% by weight of iron.

15. Process according to Claim 14, in which the silicon melt contains from 5 to 50% by weight of iron.

16. Process according to any of Claims 12 to 15, in which the silicon melt contains from 0.03 to 40% by weight of chromium.

17. Process according to any of Claims 12 to 16, in which the silicon melt contains from 1 to 40% by weight of chromium.

18. Process according to any of Claims 12 to 17, in which the silicon melt contains from 1 to 10% by weight [lacuna].

19. Process according to any of Claims 12 to 18, in which the fibres used are C fibres or SiC fibres.

20. Process according to any of Claims 12 to 19, in which the fibres are collected together to form fibre bundles and are surface-impregnated.

21. Process according to Claim 20, in which the fibres are collected together to form short-fibre bundles.

22. Process according to Claim 21, in which the fibre bundles used are formed by from about 3000 to 14,000 C filaments having mean diameters of from about 5 to 10 µm and a length of from about 2 to 10 mm.

23. Process according to Claim 21 or 22, in which the green body is produced by dry pressing or hot flow moulding of a granulated material.

24. Process according to Claim 23, in which the granulated material is produced by pan

granulation.

25. Process according to Claim 24, in which the granulated material is produced continuously or batchwise and has a mean particle size of from about 2 to 6 mm.

26. Process according to any of Claims 12 to 25, in which carbon-containing fillers, preferably carbon black or graphite, are added in the production of green body.

27. Process according to any of Claims 12 to 26, in which fillers in the form of silicides are added in the production of the green body.

28. Process according to any of Claims 24 to 27, in which a dry mixture of short-fibre bundles and fillers is first premixed and is subsequently mixed with binders in a pelletizing pan (24) to produce the granulated material.

29. Process according to Claim 28, in which the granulated material is produced from about 20-60% by weight of SiC powder, about 2-20% by weight of carbon in the form of graphite powder or carbon black, about 10-40% by weight of C fibre bundles (12K bundles) and about

15-40% by weight of a binder solution, with the latter being sprayed into a pelletizing pan (24).

30. Process according to Claim 29, in which the binder solution is an aqueous binder solution containing from 0.01 to 10% by weight of methylcellulose esters and polyvinyl alcohol.

31. Process according to any of Claims 24 to 30, in which the granulated material is dried after it has been produced and is subsequently pressed to form the green body.

32. Process according to any of Claims 12 to 31, in which the green body is heated to from about 950 to

1050°C under a nitrogen atmosphere in a pyrolysis furnace to produce the porous shaped body.

33. Process according to any of Claims 12 to 32, in which the green body is converted in the pyrolysis into a shaped body having a porosity of from about 30 to 50%.

34. Process according to any of Claims 12 to 33, in which the porous shaped body (14) is infiltrated with a silicon melt containing from about 10 to 50% by weight of iron with the balance being silicon.

35. Process according to any of Claims 12 to 34, in which the porous shaped body (14) is infiltrated with a silicon melt containing from about 10 to 50% by weight of iron, from 0.5 to 10% by weight of chromium and silicon as the balance.

Melt-infiltrated fibre-reinforced composite ceramic

The invention relates to a melt-infiltrated
5   fibre-reinforced composite ceramic containing high-
temperature-resistant fibres, in particular fibres based
on Si/C/B/N, which are reaction-bonded to a matrix based
on Si and containing at least one addition of another
material, and also to a process for producing such a
10 composite ceramic.

Such a process and such a composite ceramic are
known from US-A-5 464 655.

Carbon fibre-reinforced carbon (C/C, also known
as CFRC or in German language usage as CFC) is the first
15 industrially successful development in the group consist-
ing of fibre-reinforced composite ceramic materials.

Recently developed high-performance brake systems
based on CFRC brake discs with specially developed
friction linings, as are used, for instance, in motor
20 racing, can only be produced using numerous impregnation
or carbonization and graphitization cycles, so that the
production process is extremely time-consuming, energy-
intensive and costly and can take a number of weeks or
months. In addition, CFRC brake discs have totally
25 unsatisfactory braking properties for use in production
vehicles which are not subjected to demanding operating
conditions in the presence of moisture and at low
temperatures. This manifests itself, inter alia, in
decidedly non-constant coefficients of friction as a
30 function of the operating temperature and the surface
lining which makes regulation, as has hitherto been

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customary in 4-channel ABS systems, extraordinarily
difficult or even impossible. In view of this background,
attempts are being made to develop improved fibre-rein-
forced composite ceramic materials which can be used, for
example, as brake discs for high-performance brake
systems in motor vehicles or in railway vehicles. Fur-
thermore, such fibre-reinforced composite ceramic materi-
als are also of interest for numerous other applications,
for instance as turbine materials or as materials for
sliding bearings.

Although silicon-infiltrated reaction-bonded
silicon carbide (SiSiC) containing from 2 to 15% by mass
of free silicon has been known since the 1960s and has
also been introduced commercially for some applications
in heat engineering. Problems in respect of internal
stresses (internal stress due to cooling) occur in the
manufacture of large and thick-walled components because
of a step increase in the volume of the semimetallic
silicon when it solidifies in the microstructure of the
material. The stressing of the solidified silicon mani-
fests itself, in many cases, in the formation of
microcracks and in a reduction in adhesion at internal
interfaces, so that the strength of the material is
reduced and critical crack propagation under cyclic
thermal and mechanical stress can be expected,
particularly during prolonged use. In manufacture, the
volume expansion on solidification leads to difficulties
as have long been known when, for instance, water freezes
in closed line systems, i.e. to rupture and breaking of
the components and thus to high reject rates. In
addition, the manufacture of SiSiC materials is
relatively complicated and expensive.

US 5 079 195 A discloses a process in which a

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carbon-containing precursor body is infiltrated with a silicon melt which is alloyed with at least one element which is essentially insoluble in silicon and which forms high-melting phases, namely molybdenum, tungsten, rhe-

5 nium, hafnium, zirconium, chromium, boron and titanium. In this way, only a minimum of free silicon remains in the composite body. As a result, the risk of crack formation in the material is reduced and the heat resistance is increased, so that the material is more mechani-

10 cally and thermally stable.

EP 0 798 280 A2 discloses a composite ceramic material which is resistant to high temperatures and contains silicon carbide and molybdenum silicide.

However, a problem here is that these additives

15 are expensive and therefore unsuitable for mass production. Furthermore, these additives are unsuitable for use of the ceramic as brake disc material, since the friction pairing with customary brake linings is adversely affected.

20 It is therefore an object of the present invention to provide an improved fibre-reinforced composite ceramic containing high-temperature-resistant fibres and also a process for producing such a composite ceramic, which makes possible very simple and inexpensive produc-

25 tion of mass-produced components such as brake discs, with high thermal stability and hot strength together with sufficient oxidation resistance and thermal shock resistance being prerequisites.

The object of the invention is achieved by, in a

30 melt-infiltrated fibre-reinforced composite ceramic of the type described at the outset, the matrix containing additions of iron.

The object of the invention is completely

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achieved in this manner. According to the invention, it has been recognized that this measure makes it possible, in a particularly inexpensive and environmentally friendly manner, to avoid the volume increase which

5   occurs in the case of pure silicon and the additions of iron at the same time lead to improved braking performance in an application as a brake disc, since an improved friction pairing is obtained with conventional brake linings which are matched to brake discs based on

10   grey cast iron. Brake systems based on such brake discs are thus more readily regulated since, in addition, they are less moisture-sensitive and are insensitive to low temperatures. Furthermore, there are no critical contact pressures which have an adverse effect on regulatability,

15   as in the case of CFRC brake discs. In addition, the production process is simplified and made cheaper by the lowering of the melting point of the silicon melt by the addition of iron.

The alloying of the silicon melt used for melt

20   infiltration with iron enables the step increase in volume on solidification of a pure silicon melt to be reduced or even largely avoided. In this way, the problems caused by the stressing of the solidified silicon are avoided, a higher strength, particularly with

25   regard to cyclic thermal and mechanical stress, is achieved and at the same time the production process is simpler and less costly.

In an advantageous embodiment of the invention, preference is given to adding further additions of

30   chromium, titanium, aluminium, nickel or molybdenum in a suitable ratio as passive layer formers to a matrix based on Si which contains additions of iron. These additives can effect the formation of protective passive layers, so

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that the oxidation and corrosion resistance is improved. In this case, different coefficients of thermal expansion of the alloying components lead to stress states in the matrix which compensate for the stresses caused by the

5   fibres on cooling.

It is thus possible, according to the invention, to obtain a reaction-bonded, melt-infiltrated SiC ceramic (RB-SiC) in which the brittle Si as is present in hitherto customary RB-SiC ceramics is replaced by a phase

10 enriched with Fe or Fe together with Cr and/or Ti, Mo, Ni or Al, which leads to a significant increase in strength and ductility of the ceramic.

In a further embodiment of the invention, the matrix is produced from a silicon alloy containing from

15 0.5 to 80% by weight of iron, preferably from about 5 to 50% by weight (based on the total mass of the alloy). Since ferrosilicon in comparatively pure form is used on an industrial scale in steel production, with grades having the compositions Fe25Si75 and Fe35Si65 being

20 commercially available, a considerable reduction in the raw material costs compared with the use of pure silicon is achieved. Furthermore, there is a lowering of the melting point from about 1410°C for pure silicon to about 1340°C when Fe25Si75 is used and to about 1275°C when

25 Fe35Si65 is used.

In an additional embodiment of the invention, an additional 5-30% by weight of chromium, preferably about 7-12% by weight of chromium, based on the iron content, is added to the silicon melt which is used for melt

30 infiltration.

This change to a three-material system consisting of Si-Fe-Cr enables the iron-containing phases of the composite ceramic to be protected against corrosion and

at the same time allows the melting point to be lowered
to less than 1400°C. For this purpose, it is useful to
add at least about 7% by weight of chromium (based on the
iron content), since from about 7 to 8% by weight of

5   chromium is necessary to effect the formation of a
passive layer of chromium(III) oxide, as is known from
stainless steels. (Based on the total mass of the alloy,
the proportion by weight of chromium is preferably from
about 1 to 30% by weight, preferably from about 1 to 10%

10   by weight.) However, for cost reasons it is preferable to
select a chromium content which is not unnecessarily
high. Although the corresponding metallic starting
materials in the form of chromium-containing alloys (e.g.
FeCr) are slightly more expensive than iron silicides

15   such as FeSi ir FeSi$_2$, they give considerable advantages
as a result of the improved oxidation resistance.

     Fibres which are suitable for the fibre rein-
forcement include numerous high-temperature-resistant
fibres, in particular fibres based on Si/C/B/N and having

20   covalent bonds, with C fibres and SiC fibres being among
the best known fibres which are suitable for the ceramics
of the invention. In addition, use of, for instance,
aluminium oxide fibres is also conceivable for particu-
larly inexpensive products.

25   In an additional embodiment of the invention, the
fibres are combined to form fibres bundles and are
surface-impregnated.

     In this way, commercially available rovings and
multifilament strands (e.g. 12K bundles) can be used.

30   These are advantageously impregnated on their surface,
e.g. by means of pitch, to protect the fibre bundles
against mechanical damage during production and to avoid
excessive reaction and thus damage during the silicon

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infiltration by forming a carbon layer which can react to form SiC and thus protect the fibres.

In a further advantageous embodiment of the invention, the fibres are collected together to form short fibre bundles and can comprise, for example, C filaments having mean diameters of from about 5 to 12 μm and a length of from about 2 to 10 mm which are collected together to form fibre bundles containing from about 3000 to 14,000 filaments.

Such chopped carbon fibre bundles which are used for short-fibre reinforcement allow simplified production of a shaped body by pressing methods without costly lamination and post-impregnation having to be carried out. This makes possible inexpensive mass production and the parameters can be set so that virtually no shrinkage occurs and only minimal final machining, for example by grinding, of the finished components is necessary ("near net shape manufacture").

As regards the process, the object of the invention is achieved by a process for producing a fibre-reinforced composite ceramic containing high-temperature-resistant fibres, in particular fibres based on Si/C/B/N, which are reaction-bonded to a matrix based on Si, which comprises the following steps:

- production of a green body from fibres using binders and fillers by winding, lamination or pressing;

- pyrolysis of the green body under reduced pressure or protective gas in a temperature range from about 800°C to 1200°C to produce a porous shaped body;

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        -   infiltration of the carbonized shaped body with

            a silicon melt which contains additions of iron.

            As explained above, the volume increase which

    occurs when using pure silicon for the melt infiltration

5   (about 10% by volume) can be considerably reduced or even

    avoided by means of such additions, so that a material

    having improved properties is obtained by a simplified

    and cheaper production process.

            The internal stresses which occur in conventional

10 fibre-reinforced, reaction-bonded SiC materials (RB-SiC)

    and lead to numerous reject parts during manufacture are

    reduced or largely avoided in this way. In a preferred

    embodiment of the invention, additions of iron and, if

    desired, of chromium, titanium, aluminium, nickel or

15 molybdenum as passive layer former are mixed in suitable

    mixing ratios into the silicon melt.

            Iron additions in the range from about 0.5 to 80%

    by weight of iron, preferably from about 5 to 50% by

    weight of iron, and, if desired; chromium additions of

20 from 0.03 to 40% by weight of chromium, preferably from

    1 to 30% by weight of chromium, in particular from about

    2 to 10% by weight of chromium (based on the total mass

    of the alloy), give particularly

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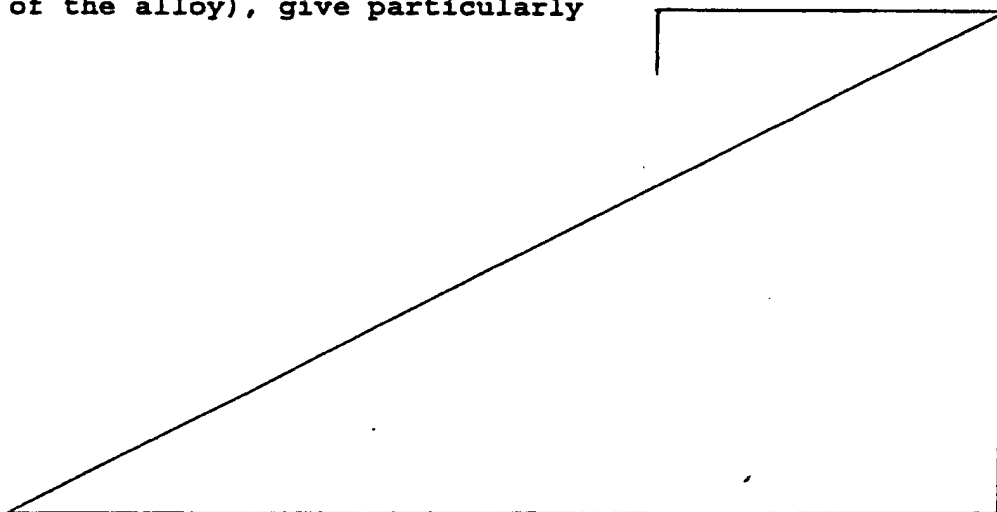
~~reduced or largely avoided in this way. In a preferred~~ embodiment of the invention, additions of iron and, if desired, of chromium, titanium, aluminium, nickel or molybdenum as passive layer former are mixed in suitable

5   mixing ratios into the silicon melt.

Iron additions in the range from about 0.5 to 80% by weight of iron, preferably from about 5 to 50% by weight of iron, and, if desired, chromium additions of from 0.03 to 40% by weight of chromium, preferably from

10   1 to 30% by weight of chromium, in particular from about 2 to 10% by weight of chromium (based on the total mass ~~of the alloy), give particularly~~ advantageous properties, a favourable reduction in the melting point and a con- siderable improvement in the oxidation resistance of the

15   iron-containing phases by formation of a passive chromium oxide layer. The abovementioned data are in each case based on the total weight of the final product.

As fibres for the production of the composite ceramic, it is possible to use any high-temperature-

20   resistant fibres, in particular fibres based on Si/C/B/N having covalent bonding, but C fibres or SiC fibres which are collected together to form fibre bundles and are surface-impregnated are among the technologically proven and commercially available fibres which, particularly

25   when used in the form of short fibre bundles comprising from about 3000 to 14,000 filaments having mean diameters of from about 5 to 12 μm and a length of from about 2 to 10 mm, preferably from about 3 to 6 mm, at a diameter of the fibre bundles of about 0.1 mm, can be employed

30   advantageously.

The green bodies from which the porous shaped bodies are produced in the subsequent pyrolysis are, in an additional embodiment of the invention, produced by dry pressing or hot flow moulding of a granulated

material which is obtained, in order to be particularly
gentle with the fibres, by pan granulation.

Pan granulation allows the mechanically sensitive
fibre bundles to be agglomerated with the other additives

5   to produce a green body in a particularly gentle and
relatively inexpensive way and at the same time achieves
a good uniform distribution.

The pan granulation can be carried out continu-
ously or batchwise, with the process preferably being

10   controlled to produce a mean particle size of from about
2 to 6 mm.

In the production of the granulated material, SiC
powder, silicides and carbon-containing fillers, prefer-
ably carbon black and/or graphite, are added in a further

15   advantageous embodiment of the invention.

Here, the preferred procedure is first to premix
a dry mixture of short-fibre bundles and fillers and
subsequently to mix this with binders and further
dissolved or dispersed additives in a pelletizing pan to

20   produce the granulated material.

It has been found to be advantageous to produce
the granulated material from about 20-60% by weight of
SiC powder, about 2-20% by weight of carbon in the form
of graphite powder and/or carbon black, and about 10-40%

25   by weight of C fibre bundles (12K bundles) which are
premixed dry and to which about 15-40% by weight of a
binder solution, based on the total initial charge of
solid materials, are added in a pelletizing pan.

Here, an aqueous binder solution containing from

30   about 0.01 to 10% by weight of methylcellulose esters and
polyvinyl alcohol has been found to be a suitable binder.

In an advantageous embodiment of the invention,
the granulated material is, after it has been produced,
first dried, preferably to residual moisture contents of

less than 10% by weight of water, and then pressed to form green bodies.

A texture which may be obtained in the pressing procedure has, if the die is configured appropriately, an advantageous effect, for instance for use as a brake disc, since the C fibre bundles are preferentially aligned parallel to the flat surface of a flat disc, which also corresponds to the main stress direction.

In a preferred embodiment of the invention, such green bodies are then heated to from about 950 to 1050°C under a protective gas atmosphere in a pyrolysis furnace or a vacuum reaction-sintering furnace to produce porous shaped bodies, preferably having a porosity of from about 10 to 50%, for a subsequent melt infiltration.

The melt infiltration which follows is preferably carried out using a silicon melt containing from about 10 to 50% by weight of iron and from about 0.5 to 10% by weight of chromium with the balance being silicon (based on the proportions by weight in the alloy).

Overall, this gives a reproducible and inexpensive manufacturing process which is suitable for mass production. Since virtually no shrinkage and internal stresses due to cooling occur, a significantly lower reject rate than in the case of conventional RB-SiC ceramics is achieved and the need for final machining is considerably reduced, particularly in the case of iron-rich phases in the microstructure.

It will be self-evident to those skilled in the art that the features mentioned above and the features still to be described below can be used not only in the combination indicated in each case, but also in other combinations or alone without going outside the scope of the present invention.

In particular, it may be mentioned that the

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process of pan granulation is suitable not only for
producing melt-infiltrated fibre-reinforced composite
ceramics containing high-temperature-resistant ceramic
fibres which are reaction-bonded to a matrix based on Si
5   and containing additions of iron, chromium, titanium,
molybdenum, nickel or aluminium, but can also be used
with considerable advantage for producing such composite
ceramics in which a pure silicon melt is used for melt
infiltration.

10   Further features and advantages of the invention
may be found in the following description of preferred
illustrative embodiments with reference to the drawing.
In the drawing:

Fig. 1   schematically shows a reaction-sintering furnace
15   for melt infiltration;

Fig. 2   schematically shows a pelletizing pan which is
         used for pan granulation, with the path of indi-
         vidual particles being indicated;

Fig. 3   shows a plan view of the pelletizing pan of Fig.
20   2 from the front side;

Fig. 4   shows an optical micrograph of the microstructure
         of a composite ceramic according to the invention
         and

Fig. 5   shows an enlarged section of the microstructure
25   shown in Fig. 4.

          A distinguishing aspect of the process of the
invention is that the final step for producing the fibre-
reinforced composite ceramic, namely the melt infiltra-
tion, is not carried out using a pure silicon melt as in

the prior art, but instead additions of iron, chromium, titanium, molybdenum, nickel and/or aluminium are added to the melt.

5   Independently of this, the porous shaped body which is impregnated with liquid metal in the melt infiltration can be produced in various ways.

        The process of the invention thus makes possible the infiltration of C hard felts and other fibre compo-sites and also the production of ceramics reinforced 2-

10   and 3-dimensionally with continuous fibres.

        The shaped bodies can thus be produced, for instance, by known lamination techniques, for example using synthetic resins, or else by pressing processes, with the green bodies being converted by pyrolysis into

15   porous shaped bodies, in particular C-bonded shaped bodies, which are permeated by a complete pore network and thus, in the subsequent melt infiltration, draw in the liquid melt by means of the capillary forces within the porous shaped body, in a similar manner to a wick or

20   sponge.

        Apart from the conventional lamination technique which, as described above, can be used for carrying out the invention, particular preference is given according to the invention to a pan granulation process for produc-

25   ing short-fibre-reinforced melt-infiltrated composite ceramics.

        The following description of the process variants for producing shaped bodies thus relates only to the production of short-fibre ceramics. However, it should be

30   stated that it is also possible to use, as an alterna-tive, conventional lamination methods.

27 168/P   - 13 -

Example 1

The starting materials used are summarized in Table 1.

Compound	Designation	Source	Data
SiC	SM93	Industriekeramik high-purity	$S_u03:3.1\ m^2/g$
Carbon black	Printex 140 U	Degussa	
Graphite	KS 6	Timcal	
Short C fibre bundles		SGL carbon	3mm, 12,000 fil.
Methyl- cellulose ester	Tylose 4000 G4	Hoechst	
Polyvinyl alcohol	Moviol 10-74	Hoechst	
FeSi(65 or 75)	FeSi75 or FeSi65	FESIL	Grain size: 5-30 mm
FeCr(65 % by mass of Cr)	Ferrochrom affine	FESIL	Grain size: 5-30 mm

Table 1

1.1 Pan granulation

In a tumble mixer, 344 g of SiC powder, 48 g of graphite powder and 8 g of carbon black were intensively mixed at 50 rpm for three hours. Subsequently, 200 g of pitch-coated short C fibre bundles were added and mixed into the powder mixture for 5 minutes at 10 rpm. This mixture was transferred to a pelletizing pan 24 as shown in Fig. 2 and 3 and subjected to a rolling-mixing motion at 30 rpm and a pan inclination angle of about 40°. 240 g of the aqueous binder solution as per Table 1 consisting of 1% by weight of Tylose 4000 G4 and 0.5% by weight of

Moviol —10-74- dissolved in demineralized water were sprayed in via nozzles from spray lines 36 for a period of 3 minutes.

In Figs 2 and 3, the paths of small particles are
5   indicated schematically by 28 and those of larger par-
ticles are indicated schematically by 34. Additional mixing can be achieved by means of an additional mixing pan 26 as shown in Fig. 3. In this method of pan granu-lation, the distribution of the components in the granu-
10 lated material being formed and also the granule size can be influenced by varying various parameters such as rotational speed and angle of inclination of the pellet-izing pan 24, rotational speed of the additional mixing pan 26, location of the spray nozzles for introduction of
15 the binder solution, type and amount of binder solution added, etc.

Overall, the pan granulation can be adjusted so that granule formation which is gentle on the carbon fibre bundles is obtained together with a uniform,
20 homogeneous distribution of the individual components. The granulated material produced preferably has a par-ticle size of from about 3 to 6 mm.

The pan granulation can be carried out either batchwise, in which case the granulated material obtained
25 is subsequently sieved to obtain the desired particle size fraction, or else can be carried out continuously as shown in Fig. 3. In this variant, dry mix is continuously introduced as indicated by the reference numeral 32 and binder solution is sprayed in via the lines 36 and, at
30 the same time, finished granulated material is discharged continuously in the region 30 of the pelletizing pan.

The granulated material formed in this way was dried to a moisture content of less than 10%.

1.2. Shaping

56.9 g of the granulated material were trans-
ferred to a pressing die having a diameter of 60 mm and
pressed to a height of 13.6 mm by means of a hydraulic
5   press using a pressure of 20 MPa. This gave a mechanic-
ally stable green body which could be transported.

1.3. Pyrolysis

The green body obtained above was taken from the
pressing die, transferred to a pyrolysis furnace and
10   heated at a rate of 10 K/min to 1000°C under a nitrogen
atmosphere. In the pyrolysis, the organic binder consti-
tuents were degraded to carbon. The resulting porous
shaped body had a weight of 55.8 g and a porosity of 39%.

1.4. Melt infiltration

15   A carbonized shaped body as obtained in section
1.3. and having a mass of 20 g was transferred to a
graphite crucible coated with boron nitride, covered with
22 g of a granulated FeSi alloy consisting of 75% by
weight of Si and 25% by weight of Fe and heated at
20   10 K/min to 1550°C under reduced pressure. This tempera-
ture was held for 30 minutes and the crucible was then
cooled to room temperature.

This procedure gave a dense, crack- and pore-free
shaped body having a density of 3.1 g/cm³ whose external
25   geometric dimensions corresponded to those of the shaped
body initially placed in the crucible.

Instead of placing the shaped body directly in a
graphite crucible 20 coated with boron nitride, an
alternative possibility is, as shown in Fig. 1, to use a
30   porous SiC charging plate 16 in the furnace chamber 12 of
a reaction-sintering furnace 10; this SiC charging plate
16 stands on feet 18 in the melt 22 of the graphite

crucible 20 coated with boron nitride or is connected
therewith via porous wicks. In this variant, a larger
amount of granulated material for producing the melt 22
can be introduced into the crucible 20 since the melt 22
5   rises from below through the porous feet 18 and the
porous charging plate 16 into the shaped body 14.

Example 2

      A green body was produced as described above by
pan granulation and subsequent pressing and subjected to
10   pyrolysis in the above-described manner in a pyrolysis
furnace.

      The shaped body obtained in this way and having
a mass of 20 g was again transferred to a graphite
crucible coated with boron nitride, covered with 22 g of
15   a mixture of 19 g of a granulated FeSi alloy consisting
of 75% by weight of Si and 25% by weight of Fe to which
3 g of granulated FeCr (65% by weight of chromium) had
been added and the crucible was heated at 10 K/min to
1700°C under reduced pressure. This temperature was held
20   for 30 minutes. The crucible was then cooled to room
temperature.

      This procedure gave a dense, crack- and pore-free
shaped body having a density of 3.2 g/cm³ whose external
geometric dimensions corresponded to those of the shaped
25   body initially placed in the crucible.

      Figs 4 and 5 show optical micrographs of polished
sections of specimens which were produced as described in
Example 1.

      In Fig. 4, a C fibre bundle can be seen in the
30   left-hand half of the picture while part of the next C
fibre bundle is visible at the bottom right-hand corner
of the picture. The numeral 40 denotes carbon formed by
pyrolysis while the numeral 42 denotes C fibres.

Secondary SiC formed from the reaction of carbon fibres
with silicon is present at the edge of the C fibre
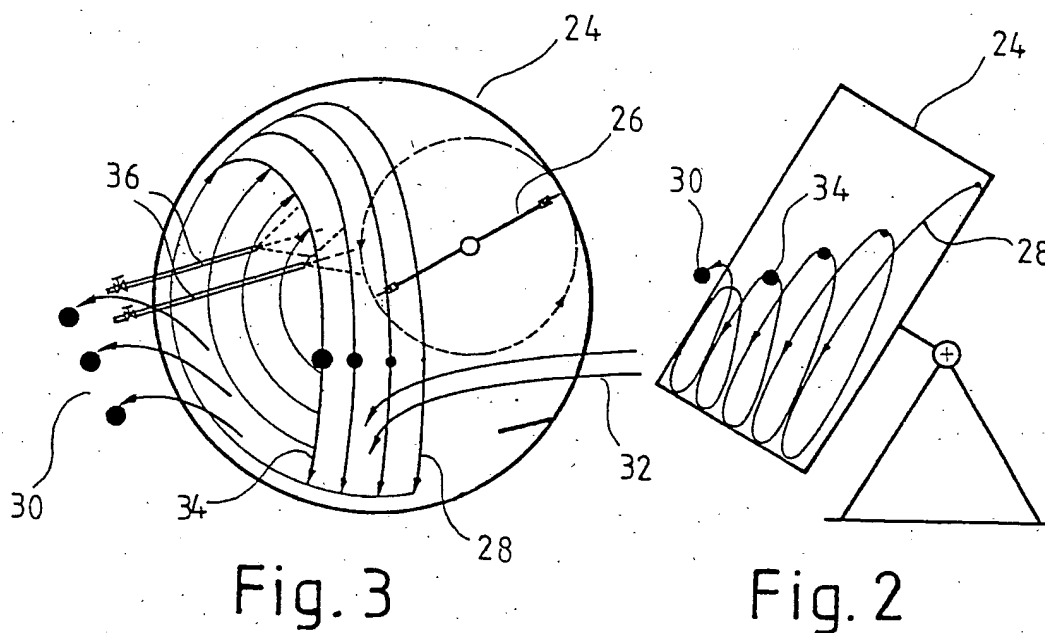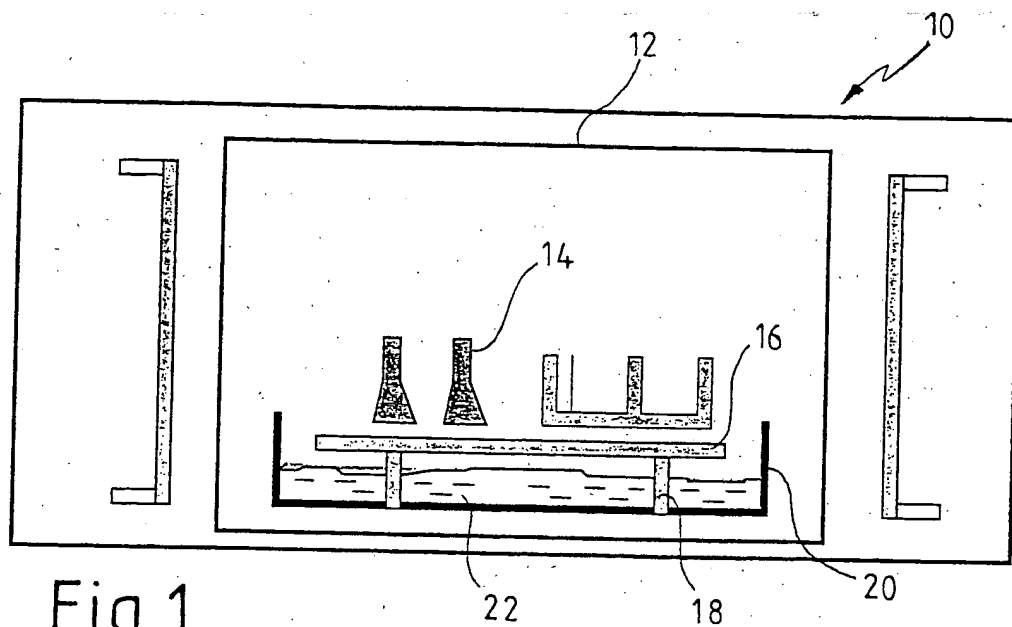bundle; this secondary SiC is denoted by the numeral 48.

The light-coloured phase denoted by the numeral
5   44 is silicon or Si/Fe/Cr. The dark grey phase denoted by
46 is SiC.

In the enlarged view shown in Fig. 5, in which a
carbon fibre bundle is cut virtually perpendicularly
across, the individual C fibres can readily be seen. The
10   secondary SiC which has been formed from the reaction of
C fibres and is denoted by the numeral 48 can also be
readily seen.

It can easily be seen that the carbon fibre
bundle is retained virtually unscathed and only a few of
15   the C fibres in the outer region have been converted into
secondary SiC.

This explains the considerable increase in
strength which is achieved by the gentle treatment of the
C fibre bundles in the pan granulation and in the subse-
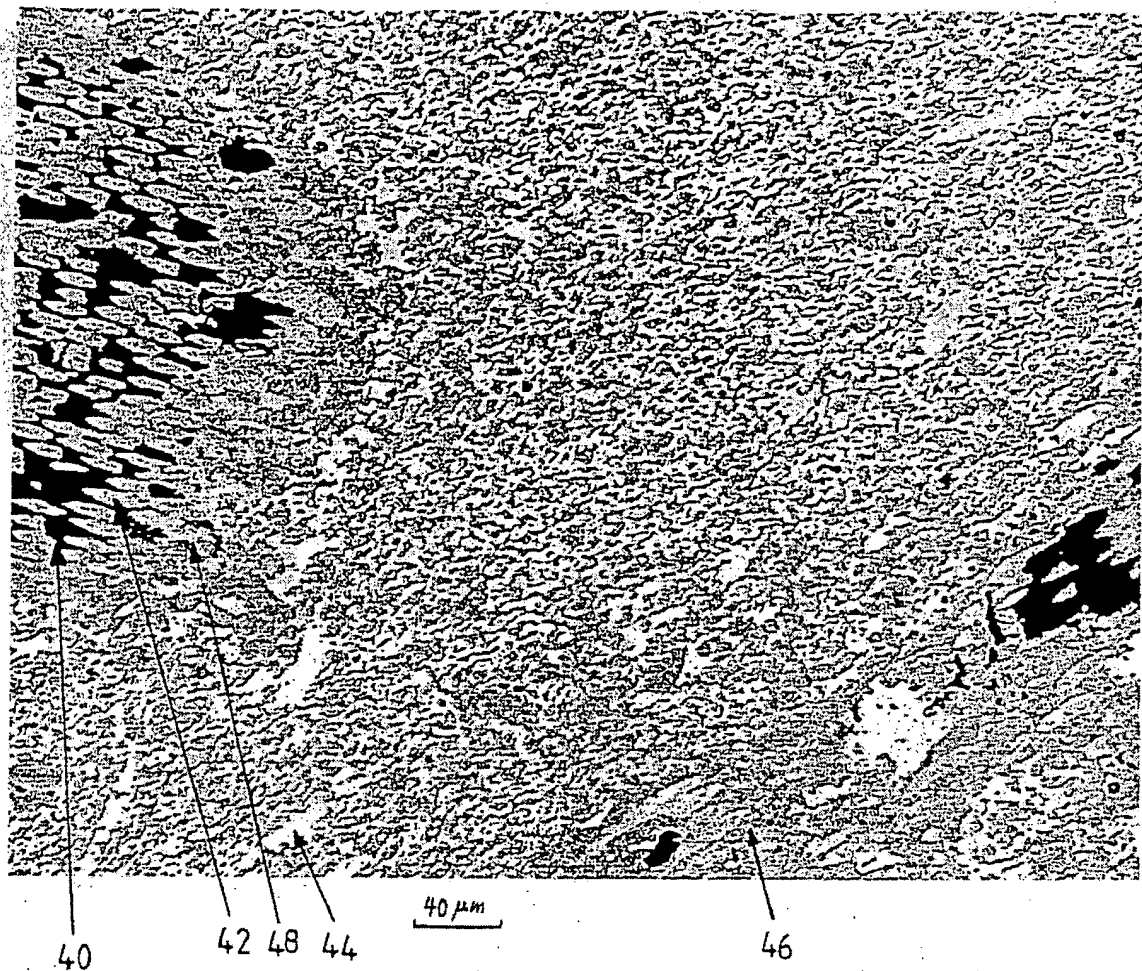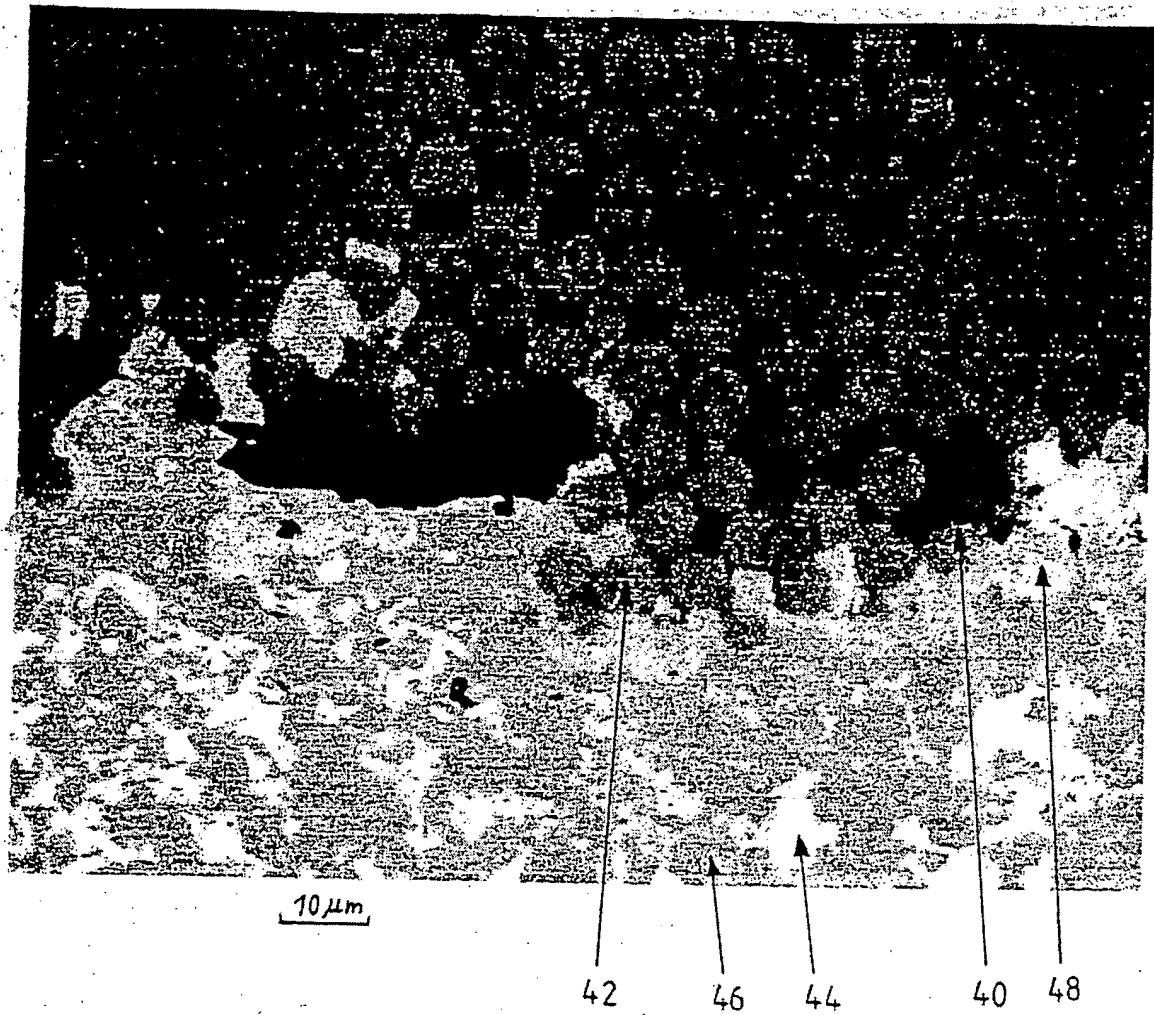20   quent process steps.

Fig.1

Fig. 3

Fig. 2

40   42 48 44 $\underline{40\,\mu m}$ 46

Fig. 4

10 μm

42   46   44   40   48

Fig. 5

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NEW LOW TEMPERATURE PROCESSING FOR BORON CARBIDE/ ALUMINUM BASED COMPOSITE ARMOR

FINAL REPORT

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U. S. ARMY RESEARCH OFFICE

DAAL 03-88-C0030

THE DOW CHEMICAL COMPANY

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
	Approved for public release;
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
	ARO 26166.1-MS-A

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
The Dow Chemical Company CR-Advanced Ceramics Lab		U. S. Army Research Office

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Midland, MI 48674	P. O. Box 12211 Research Triangle Park, NC 27709-2211

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
U. S. Army Research Office		DAAL03-88-C-0030

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
P. O. Box 12211 Research Triangle Park, NC 27709-2211	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

New Low Temperature Processing For Boron Carbide/Aluminum-Based Composite Armor

12. PERSONAL AUTHOR(S)
Aleksander J. Pyzik, P. Douglas Williams, Ann McComps

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 10-1-88 TO 3-31-90	1990, June 1	41

16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Lightweight armor, B4C/Al Cermets, Rapid Omnidirectional
			Compaction, Dispersion of B4C and Al powders, B-C-Al Phases

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The developed B4C/Al based materials are a promising alternative for the use in lightweight armor application. The advantage of B4C/Al composite over the traditional metal armor is its ballistic limit of 80 to 90% of that for hot pressed B4C, thus similar to ceramics such as AlN or SiC. The advantage of B4C/Al over monolithic ceramic armor is its higher toughness. The ballistic efficiency of B4C/Al materials, relative to hot-pressed boron carbide, was found to be directly related to the initial boron carbide content, the B-C-Al phases formed in situ, and their continuity. The highest improvement of ballistic efficiency was associated with increasing contents of B4C and AlB2 in the system.

The Rapid Omnidirectional Compaction process is a suitable technique to produce nearly dense B4C/Al cermet at the low temperature. Dense, but soft, cermets can be near-net shaped and then changed into hard, ceramic-like structure through heat-treatment. Mechanical properties of B4C/Al cermets depend mostly on the concentration and continuity of the boron carbide phase. Colloidal processing and post densification heat-treatment can be used to

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete   UNCLASSIFIED

19. further modify properties for the application at hand.

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INTRODUCTION

Boron carbide/aluminum composites combine a ceramic's hardness, stiffness, and low density with a metal's ability to dissipate tensile stress. One of the limitations of any B_4C/Al cermet fabrication process is that the starting composition must always have an excess of metal. In order to produce armor materials, this metal must be depleted by formation of various binary and ternary phases. Depending on the extent of heat-treatment. 20 to 40 % of the material will consist of these new phases. It is not surprising therefore, that these phases play a critical role in the mechanical behavior of the composite, and one would expect that the ballistic performance of these multi-phase composites would vary greatly, depending on material chemistry.

The objective of this work was to develop the ability, starting with a given powder composition, to vary the fabrication conditions in such a manner that a series of B_4C/Al materials with controlled chemistry could be produced. The tests conducted on these materials resulted in determination of the ballistic limits for B_4C/Al materials as well as in the optimization of the material chemistry with respect to ballistic behavior.

With the Rapid Omnidirectional Compaction process, employed in this work, densification of boron carbide and aluminum is done near the melting point of aluminum, suppressing the formation of a low temperature phases and eliminating formation of high temperature phases. Thus, one can fabricate the cermet by ROC with minimal formation of B-C-Al phases, and then post-heat treat to form multi-phase ceramic-like structures with variety of designed compositions.

In the ROC fabrication technique two basic types of B_4C/Al materials can be made. The first with isolated B_4C grains in the multi-phase ceramic-metal matrix and the second with continuous phases of ceramic and metal. Both processes, described in detail in Appendix A, have similar basic processing stages. The "preforms" are densified into parts by heating them to a temperature near the melting point of aluminum in a composite fluid die material, and then by applying pressure to them for less than one minute. The "fluid" glass die exhibits plastic flow at the temperature and presure of densification. The die walls function as incompressible fluid elements, which transmit an isostatic pressure of up to 120 ksi to the part.

Obtaining dense B_4C/Al materials requires development of processing procedures, including mixing of ceramic and metal powders, formation of greenware, sample encapsulation and degassing, and densification under rapidly applied high pressure. Therefore, the research concentrated on the following areas:

1

1.0. PREPARATION AND PROPERTIES OF ROCED CERMETS

The objectives of this portion of the project were (i) development of dry and wet powder processing methods for mixed powder greenware fabrication, (ii) preparation of dense cermet with greater than 70 v/o inital ceramic content, and (iii) incorporation of non-reactive TiB_2 in B_4C/Al cermets.

1.1 Preparation

Since densification of B_4C/Al composites by ROC depends upon liquid metal assisted rearrangement of the ceramic particles, intimate mixing and packing of the powders was considered to be an important goal of the project. Both dry mixing and wet mixing processes were studied.

A description of the powders used in this program is given in Appendix A. Boron carbide powder was typically in the 0.1-3.0 µm diameter range (~1 µm median diameter). A high packing density boron carbide powder with a particle size range of 0.1 to 15 µm was used in some cases. The aluminum powder was finer than 325 mesh (nominal 4 µm diameter). The titanium diboride powder also had a median particle diameter of 4 µm.

Dry mixing was accomplished by combining powders in a plastic bottle with the complex rotating and tumbling motion of a Turbula Mixer (Glenn Mills, Inc.). Green pucks were pressed without binder and processed as described in Appendix A. Mixing times were optimized by qualitative inspection of parts after densification.

Development of a colloidal casting formulation for codispersed B_4C and Al powders has already been reported (see Appendix B). Toluene was chosen as the mixing medium in order to avoid the oxidation of Al powder that was expected in water and alcohols. A variety of short chain and polymeric additives were evaluated by sedimentation, viscosity, and filtration rate experiments for the codispersion of the B_4C and Al powders in 70:30 volume ratio. Sedimentation experiments indicated that the dispersion stability of fine B_4C powders was much more sensitive to the additive used than was the stability of the coarse TiB_2 and Al powders. All dispersants suitable for B_4C were also found to be suitable for the mixed dispersions.

Modelling of the pressure casting process by filtration theory indicated that 70:30 B_4C/Al filter cakes were incompressible below 50 psig. The filtration rate was about 5 times faster for an agglomerated suspension with Adogen 172D oleylamine than for a dispersed suspension with Hypermer KD3 polymeric dispersant, but the casting density was about 5-10% lower. Casting times for a 1.25 cm thick part were 5.5 and 33 min, respectively at 50 psig. Extrapolation of these data to a casting pressure of 500 psig predicts casting times of less than 15 min for 2.5 cm cakes, assuming that the cakes remain incompressible at this pressure.

1.2 Properties

Some degree of residual porosity (typically 1-2%) was evident in all of the ROCed composites. Parts prepared with varying B_4C content (see below) indicated that porosity was not noticably sensitive to the ceramic loading and was, therefore, not due to packing limitations of the ceramic powder. Possible reasons for this porosity are: (1) gas formation during the ROC cycle, and/or (2) formation of incompressible agglomerates from B_4C + Al reactions during the heating steps prior to ROC.

Gas formation was a significant problem in early densification experiments. Bloating and rupturing of the containment cans was frequently observed after part recovery if a hot vacuum outgassing step was not performed before ROCing (see Appendix A for experimental details). Significant H_2O and CO_2 evolution was shown to occur in TGA/MS analysis of B_4C and B_4C/Al powder compacts when heated from 25 to 650°C. The extent of gas formation depended primarily on the oxygen content of the B_4C powder and the atmosphere, and could not be entirely eliminated without resorting to very high purity non-oxidizing atmosphere, particularly above 400°C. Organic dispersants were shown to be volatilized after a single burnout cycle and were not responsible for the gas formation observed during ROC. Although gas formation was minimized by incorporation of the hot vacuum outgassing step, it has not been discounted as a cause for microstructural porosity.

It was found early in this work that reactions between B_4C and Al begin at temperatures as low as 450°C to form Al_4BC and other phases. These reactions could cause formation of rigid agglomerates prior to ROC and prevent full densification. Although the effect of reaction phases on densification has not been systematically evaluated, control of ceramic-metal reactions at low temperatures is likely to be the key to elimination of residual porosity in these materials.

The effects of different greenware processing methods on mechanical properties are indicated by the first 3 samples in Table 1. The well dispersed, wet mixing formulation with Hypermer KD3 polymeric

Table 1. Properties of ROCed Composites with 30 v/o Al Before Heat Treatment.

Sample	Density (g/mL)	Hardness (Rockwell A)	Flex Strength
70/30 B_4C/Al/dry	2.62±.03	81±3	57±5 ksi
70/30 B_4C/Al/wet/A	2.57±.02	77±5	45±20 ksi
70/30 B_4C/Al/wet/B	2.56±.02	74±5	70±10 ksi
49/21/30 B_4C/TiB_2/Al/wet/B	2.94±.01	73±5	73±15 ksi
63/7/30 B_4C/TiB_2/Al/wet/B	2.71±.01	74±5	65±12 ksi

dispersant (designated "B") gave parts with moderately higher strength than dry mixed formulations or agglomerated wet mixed formulations containing Adogen 172D oleylamine (designated "A"). Surprisingly, however, lower hardness and density were obtained with both of the wet mixed parts than with dry mixed materials.

Addition of TiB_2 particulates to the composites had no significant effect on the properties reported in Table 1. Note, however, that these data are for samples which were not heat treated after densification. Because TiB_2 is not reactive with the phases in B_4C/Al composites, one would expect heat treatment to have a different effect on TiB_2 and non-TiB_2 containing materials (see next section). Heat treatment experiments have not yet been performed for TiB_2 composites.

A high purity, high packing density B_4C powder was used to prepare B_4C/Al composites with >70 v/o initial ceramic content (see Appendix A). Greenware were prepared by wet mixing and slip casting with the Hypermer KD3 formulation. The packing limit for this B_4C powder was approximately 80 v/o. A sample made with an initial composition of 90/10 B_4C/Al was was found to have a final Al content of 20 v/o due to intrusion of the metal can during ROC. Subsequent evaluation of the part revealed cracks which had been filled with molten metal during densification. Samples with initial compositions of 70/30 and 80/20 B_4C/Al densified without significant intrusion of Al. The Rockwell A hardness increased from 74 to 77 with increasing ceramic content, while flex strength was relatively unaffected (83±5 ksi for 70/30 vs. 78±3 ksi for 80/20). Microstructural porosity in the 2-20 µm diameter range was observed in all of the compositions, independent of ceramic loading.

2.0. HEAT-TREATMENT OF DENSE B_4C/AL CERMETS

The main objectives of the heat-treatment experiments were (i) determination of the conditions at which B-C-Al phases can be formed, and (ii) establishing the effect of these phases on static and ballistic properties.

The major phases influencing mechanical properties of B_4C/Al based materials are Al_4BC, AlB_2, $AlB_{24}C_4$ and Al_4C_3 (Appendix C). Since the formation of $AlB_{24}C_4$ is associated with the existence of undesirable Al_4C_3, the heat-treatment should be limited to temperatures below 1000°C. At these temperatures AlB_2 and Al_4BC form the dominant phases. Heat-treatment conducted at temperatures between 600°C and 700°C produces mainly AlB_2, while heat-treatment at 900°C to 980°C gives mainly Al_4BC. Heat-treatment between 700°C and 900°C results in materials with mixture of AlB_2 and Al_4BC.

In order to produce samples for heat-treatment experiments, boron carbide powder was dry mixed with aluminum powder and ROCed or partially sintered prior to the ROC pressure infiltration (see Appendix A). It has been established that an increase in hardness of B_4C/Al composites depends on the kinetics of Al_4BC formation and the Al_4BC to AlB_2 ratio. At temperatures below 1000°C, the maximum hardness of 88 (Rockwell A scale), is achieved after about 20 hours of heat-treatment. The flexure strength of B_4C/Al materials depends on the continuity of the boron carbide phase (see Appendix C). A reduction in flexure strength was observed in all B_4C/Al materials experiencing heat-treatment above 600°C. It is believed that this reduction was not due to the properties of some specific phases, but rather to the phenomena associated with the process involving the growth of new phases. The increase of fracture toughness was observed only in B_4C/Al based materials with isolated grains of boron carbide. This increase was associated with densification of metal phase. The formation of ceramic phases reduces toughness in a way that depends on the type of phase formed. AlB_2 is least detrimental to the fracture toughness of B_4C/Al materials.

3.0. BALLISTIC EVALUATION

The main objective of ballistic screening was to determine potential applicability of B_4C/Al cermets for lightweight armor against small caliber threats.

The ballistic screening experiments indicate that the ballistic limit of B_4C/Al materials is directly related to the initial content of boron carbide concentration, type of phases formed in the system, and continuity of ceramic phase. It has been found that ballistic limit

increases when the amount of B_4C, AlB_2 and/or Al_4BC increases. In contrast, formation of $AlB_{24}C_4$ and Al_4C_3 was detrimental to ballistic properties. The higher the initial boron carbide content, the higher the ballistic efficiency, approaching 90% of that for hot-pressed boron carbide. The highest ballistic ratio was observed in materials containing about 80 v/o of boron carbide. B_4C/Al cermets with 70 v/o of initial boron carbide content showed ballistic efficiencies ranging from 70 to about 80%, depending on chemistry. The 10 and 30 v/o replacement of boron carbide by TiB_2 resulted in materials with slower metal depletion reactions. Because of the greater amount of residual metal, heat treated TiB_2-containing composites had ballistic efficiencies between 72 and 74% relative to hot pressed B_4C and similar to that of nonheat-treated B_4C/Al cermets. At high ceramic content, B_4C/Al materials with connected boron carbide phase showed typically 2 to 3 percent higher ballistic ratio than B_4C/Al cermets with boron carbide grains isolated in multi-phase matrix. In the latter case, the largest contribution came from AlB_2, which plastically deformed under high impact. Although, the chemistry and the continuity of ceramic phases were found to play important roles, no strong correlation between static mechanical property and ballistic performance was observed.

4.0 GRADIENT STRUCTURES

Since the ROC process allows one to densify combinations of dissimilar materials in one structure, the objective was to develop a practical process to make gradient structures of armor scale.

In order to take advantage of the full range of properties of B_4C/Al composites, a gradient composition was desired in which hard, low metal content cermet layers would be backed by tough, high metal content cermet. Pressure filter casting of stacked B_4C/Al compositions was chosen over stacked tape cast structures due to the anticipated difficulty of removing a large amount organic binder from thick armor structures. A gradient structure of five discontinuous layers which ranged from 70 v/o to 30 v/o B_4C (nominal) in a 2.5 cm thick tile was demonstrated. Samples have not been prepared for ballistic evaluation at this time.

Gradient structures were made by successive pressure casting of 0.5 cm thick layers of B_4C/Al in a stainless steel pressure filter (see Appendix A). After ROC, about half of the gradient parts had laminar cracks between the 70/30 and 60/40 B_4C/Al layers. The cause of the cracks has not yet been determined, but it is likely that they formed before or during ROC since they were filled with metal. Polished cross sections of the gradient parts had composition dependent Rockwell A hardnesses of 74 ± 2 (70/30), 71 ± 1 (60/40), 67 ± 2 (50/50), 58 ± 2

(40/60), and 47±3 (30/70). Residual porosity in the 2-20 μm diameter range was evident in the microstructure of all layers, independent of ceramic content. This observation indicates that the porosity was not due to insufficient packing efficiency of the boron carbide powder.

CONCLUSIONS

Research performed under BTI/DARPA contract DAAL 03-88-C0030 on development of B_4C/Al based composite armor allows the following conclusions to be made.

1. The developed B_4C/Al based materials are a promising alternative for the use in lightweight armor application. The advantage of B_4C/Al composite over the traditional metal armor is its ballistic limit of 80 to 90 % of that for hot pressed B_4C, thus similar to ceramics such as AlN or SiC. The advantage of B_4C/Al over monolithic ceramic armor is its higher toughness.

2. The ballistic efficiency of B_4C/Al materials, relative to hot-pressed boron carbide, was found to be directly related to the initial boron carbide content, the B-C-Al phases formed in situ, and their continuity. The highest improvement of ballistic efficiency was associated with increasing contents of B_4C and AlB_2 in the system. At the same time no strong correlation between ballistic performance and mechanical properties (i.e., fracture toughness, flexure strength, hardness, or modulus) was observed.

3. The Rapid Omnidirectional Compaction process is a suitable technique to produce nearly dense B_4C/Al cermet at the low temperature. Dense, but soft, cermets can be near-net shaped and then changed into hard, ceramic-like structure through heat-treatment.

4. Mechanical properties of B_4C/Al cermets depend mostly on the concentration and continuity of the boron carbide phase. Colloidal processing and post densification heat-treatment can be used to further modify properties for the application at hand.

ACKNOWLEDGEMENTS

test samples. We also thank Don Beaman, Dave Susnitzky, and Charlie Wood for electron microscopy. Special thanks to Alan Hart, Bruce Peters, and Jim Mackl for their support and encouragement.

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PRESENTATIONS

1. A.J. Pyzik, " The Effect Of Heat Treatment On Properties Of B_4C/Al Cermets", 3rd Internat. Conf. Ceram. Powder Process. Sci., February 4-7, 1990 (San Diego, CA).

2. A.J. Pyzik, J. Ott, K. Groves, and A. McCombs, " High Impact Behavior Of B_4C/Al Cermets", 92nd Annual Meeting of American Ceramic Soc., April 23, 1990, Dallas, TX.

Appendix A
EXPERIMENTAL CONDITIONS

POWDERS

The boron carbide powder used in most of this work was prepared on a developmental scale by a carbothermal process at The Dow Chemical Company and attrition milled to a size between 0.1-3.0 μm. Major impurities were <1 w/o free graphitic carbon, 1.0-1.5 w/o oxygen, 0.4 w/o nitrogen, 160 ppm calcium, 140 ppm chromium, 270 ppm iron, and 330 ppm nickel. The surface area was 7 m^2/g. Initial dispersion and filter casting studies used Tetrabor® 1500 B$_4$C powder from Elektroschmelzwerke Kempten ("ESK", Munich, FRG), which had physical and chemical properties very similar to those of the Dow powder. The powder obtained from ESK was supplied as 20-80 μm spherical (spray dried) agglomerates which made it undesirable for use in the dry mixed powder preparations. Subsequently, a premium grade, high purity B$_4$C powder became available from ESK which could attain a packing density of 70-80% of theoretical. This powder was used in the preparation of high ceramic content composites.

Titanium diboride was obtained from Union Carbide (HCT-F grade, nominal 4 μm diameter) with a surface area of 0.74 m^2/g. Major impurities were 0.42% carbon, 0.81% oxygen, and 270 ppm iron.

The aluminum powder, Alcan 105 grade, was a >325 mesh (nominal 4μm diameter) powder of >99% purity. Impurities (from neutron and X-ray analyses) included oxygen (0.7%), iron (0.2%), and silicon (0.1%). The surface area was 0.54 m^2/g.

All powders as supplied by the manufacturers were stored under N$_2$ atmosphere as a precaution, but could be kept in ambient atmosphere for months with less than a 0.1 w/o change in oxygen content.

MIXING AND FORMING

Dry Method

All dry powder processing used developmental boron carbide made at Dow since the spray dried agglomerates in the ESK powder were not easily broken down during mixing. Boron carbide and aluminum powders were weighed in the desired ratio (usually 70:30 by volume) and screened (35 mesh ASTM) in a nitrogen-filled glove box in order to protect the metal powder from ambient atmosphere during agitation. The blend was loaded into a polypropylene bottle under N$_2$ and tumbled with a Turbula T2C mixer from Glenn Mills, Inc. The blend was periodically removed and screened (35 mesh ASTM) to break up agglomerates generated during mixing. Total mixing time was 4 to 6 h. Binder addition was not necessary to obtain whole dry pressed parts.

Greenware was formed at 33.2 ksi in a Dake press with 3.505" diameter die. Part thickness was typically 1/2". The pressure was held for 10-15 minutes in order to de-air and reduce "spring-back" of the compact. Samples were then baked out under vacuum at 510°C for 4 h.

Wet Method

ESK Tetrabor 1500 B_4C powder was used in the dispersion and filtration rate experiments, while the internally prepared B_4C was used to make parts for ROC and subsequent property measurement. Both powders behaved similarly in the dispersion and casting process. Pucks with the composition 70/30, 80/20, and 90/10 (v/o) B_4C/Al were cast with the high packing fraction B_4C powder from ESK.

A detailed description of the casting formulations and procedures has been reported (Appendix B). Dispersions for casting were typically prepared by stirring designated amounts of B_4C, TiB_2, and Al powders into the dispersant/toluene solution to obtain 40 v/o total solids. Ultrasonic agitation (800 watts, 2.5 cm horn) and slow roll milling with SiC media were used to disperse and mix the powders. Pucks with 7.0 cm diameter were cast in a pressure filter at 50 psig. Parts of smaller or larger dimension were slip cast into covered PTFE rings on flat plaster molds. Thin (0.4-0.5 cm) cross sections of 1.5-2.0 cm thick slip cast parts were analyzed by X-ray diffraction, BET surface area, and %C, and gave no evidence for compositional gradients due to preferential settling of powders during casting. This was in spite of the fact that slip casting on plaster could take as long as 4 h for the Hypermer KD3 formulations.

Filter cast parts were dried at 45°C in air and then baked out under flowing N_2 at 500°C to remove organic additives.

DENSIFICATION

B_4C/Al Materials With B_4C Isolated In Multi-Phase Metal Matrix

Baked out greenware were enclosed in fitted cans of low carbon steel or 1100 aluminum; internal spaces between the can and the parts were filled with 1100 aluminum thin sheets and pellets. Steel cans were made slightly oversized in order to allow extra aluminum fill material to be placed between the part and the wall of the can. A metal stem was attached to a hole in the top of each can for vacuum outgassing. Canned parts were evacuated at ambient temperature for >12 h and then heated to 100, 300, and 610°C, successively, such that < 25 µm Hg pressure was attained at each temperature. The parts were cooled to ambient and the stems were sealed under vacuum.

Each sealed part was loaded into a separate fluid die and surrounded with glass pocket medium at ambient temperature. The fluid die assemblies were heated to between 655-660°C under N_2 as quickly as possible (2-3 h) to minimize $Al_xB_yC_z$ phase formation. The dies were then transferred to the ROC press and compacted at 120 ksi for 30 sec. Parts were broken out of the glass after cooling and milled out of the metal containers.

B_4C/Al Materials With Continuous Ceramic And Metal Phases

In general, the processing is similar to that for the isolated B_4C matrix, except that a sintered, porous body must first be formed from a particulate ceramic powder. The sintered, porous boron carbide body is placed in contact with the metal and heated to about 680°C to 700°C. After pressure is applied, liquid metal is forced into ceramic and fills the voids.

PROPERTY MEASUREMENT

Reported final densities were the average of the indivdual densities determined from the weights and geometric volumes of 4 point bend bars. Percent total aluminum was determined by X-ray fluorescence from a 3/8" diameter circular area on a flat cut surface of the cermet. Sample counts were calibrated by reference to an NBS standard Al sample containing Fe and Si. Four point bend tests and specimens (3 mm X 4 mm X 45 mm) were in accordance with the military specification MIL STD 1942. A minimum of 10 bars from each sample were tested. Hardness was tested using Rockwell A scale and 13.3 kg load.

BALLISTIC TESTING

Concurrent with the development of the processing technology, ballistic testing was carried out to monitor the effect of several variables on the ballistic behavior of the cermet products.

The ballistic screening was done with a two shot limiting velocity test (Vbl). The testing was carried out at University of Dayton Research Institute ballistic range. Limiting velocities were obtained to within 50 feet/sec when possible. The test projectile was a simulated .30 cal AP round (Rc=54). Targets (0.33 inch thick) were constructed by mounting the experimental tile, with epoxy resin, directly onto a 0.25 inch 6061 aluminum plate. The ballistic criteria used to evaluate test results were based on a direct comparison to hot-pressed ceramic armor tile. This comparison is reported in the form of ballistic

efficiency, i.e. the ratio of the areal density of hot-pressed boron carbide at 2700 fps to the areal density of the experimental tile at 2700 fps, as determined from the experimental Vbl.

APPENDIX B
COLLOIDAL PROCESSING AND CASTING OF B$_4$C/AL GREENWARE
P. Douglas Williams and Yi-Bin Huang

COLLOIDAL PROCESSING AND CASTING OF B$_4$C/Al GREENWARE

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The codispersion of fine boron carbide and aluminum powders in toluene was studied with a variety of surfactants. Dispersion stability was dominated by the higher surface area powder, which was B$_4$C in this case. Short chain amine surfactants were generally effective in reducing the sedimentation volume of B$_4$C in toluene, but still exhibited flocculated suspension characteristics (rapid settling, clear supernatant). Two polymeric dispersants were identified which yielded well dispersed, slow settling dispersions of B$_4$C. Casting of concentrated B$_4$C/Al powder dispersions (70:30 vol ratio, 40 v/o total solids) in a pressure filter at 138-345 kPa (20-50 psig) indicated that the filter cake permeability was insensitive to filtration pressure in the range studied, except when the casting rate was slow enough for sedimentation to be observed. Wet cake density was found to be sensitive to the type of additive, ~50% of theoretical for short chain surfactants and ~60% of TD for polymeric surfactants. Parts prepared from well dispersed formulations appeared to be stronger and more reliable after densification than those prepared from weakly flocculated systems.

INTRODUCTION

Tough B$_4$C/Al composites are attractive for structural, wear, and armor applications which require high modulus and low density.[1] The ability to prepare these composites with different B$_4$C/Al ratios and with a connected or disconnected ceramic phase microstructure allows a wide range of properties to be obtained.[2] In addition, reactions between the ceramic and metal phases can be exploited by annealing the dense cermet. Proper depletion of the Al and B$_4$C phases to form ternary Al$_x$B$_y$C$_z$ compounds yields materials with higher hardness and modulus.

B$_4$C/Al composites can be prepared by molten metal infiltration of porous green and sintered bodies or by a novel pressure densification process known as Rapid Omnidirectional Compaction (ROC).[3] Although recent patents have indicated improvement,[4] bulk infiltration processing is typically slow and limited in practical application to parts of < 2 cm thickness. Also, since infiltration requires temperatures above 1000°C, the formation of ternary Al$_x$B$_y$C$_z$ phases can be extensive, particularly in thick samples with long processing times. In order to optimize the

mechanical properties of the composite, it is desirable to control the formation of ternary phases.

ROC processing allows the isostatic compaction of thick B_4C/Al parts below 1000°C with better control of ternary phase formation and shorter processing time than infiltration.[5] The ROC densification of B_4C/Al composites proceeds by molten metal assisted rearrangement of the ceramic particles.[6] In order to successfully prepare dense cermets with high ceramic content (> 60 v/o) by ROC, the ceramic powder must have a high packing efficiency and must be well mixed with the metal phase. Filtration or slip casting provides excellent mixing and greenware packing, but requires a formulation in which both of the constituent powders are well dispersed.[7] This report describes the dispersion properties of fine boron carbide and aluminum powders in toluene and the analysis of their casting behavior by filtration theory. Bend strength data is presented for dense B_4C/Al parts cast from weakly flocculated and well dispersed casting systems.

EXPERIMENTAL

The boron carbide and aluminum powders in this study were used without modification.* Reagent grade toluene from Fisher Scientific was used without purification. Dispersants were used as obtained from commercial sources.** Oxygen and nitrogen analyses were obtained by fluxing a powder sample in a LECO EF-100/TC-136 electrode furnace / thermal conductivity detector. Carbon analysis was obtained by combustion in a LECO HF-100/IR-212 induction furnace / infrared detector system. Percent free carbon (as graphite) was determined from the ratio of the integrated X-ray diffraction peaks for graphite and boron carbide.[8] Particle size analysis was obtained by centrifugal sedimentation of a dilute (< 0.1%) dispersion of powder in neutral distilled water (Horiba CAPA-700).

Gravity sedimentation experiments were performed with 5 v/o solids dispersions. Powders were added to the dispersant/toluene solutions and agitated ultrasonically (300 watt, 2 cm horn) for 30 sec in a 50 mL beaker. The dispersions were then quickly transferred to a 25 mL graduated cylinder and stoppered. Some dispersants with slow powder adsorption rates (e.g. Acryloid B-99), yielded lower sediment volume when stirred for several hours between sonication and sedimentation. The cylinders were allowed to stand at ambient temperature without disturbance for at least 24 h before the final sedimentation volume was recorded. Viscosity was recorded at ambient temperature with the small sample adapter spindles #18 or #31 on a Brookfeld Rheoset LVRH Viscometer. Viscosities and shear rates were calculated from the spindle constants supplied by Brookfield Engineering.

Dispersions for casting were prepared by stirring the B_4C and then the Al powders into the dispersant/toluene solution to obtain 40 v/o total solids. Ultrasonic agitation (800 watts, 2.5 cm horn) was sufficient to remove visible agglomerates

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* TETRABOR® 1500 boron carbide was obtained from Elektroschmelzwerke Kempten ("ESK", Munich, FRG). Alcan 105 aluminum powder was from Alcan-Toyo America, Inc. (Joliet, IL).
** See the Appendix for a list of suppliers.

and leave a smooth, dry film on a spatula tip. The dispersion was then roll milled for at least 16 h in a 450 mL wide mouth polypropylene bottle with 75 g of 5 mm diameter SiC balls. Pucks were filter cast on a 0.2 μm pore size PTFE membrane* in a stainless steel pressure filter.** A cylindrical 70 mm ID stainless steel insert was made and sprayed with a fluorocarbon polymer film to make part removal easier. Casting was carried out under 138-345 kPa (20-50 psig) of N_2. During casting, the filtrate was collected in volumetric glassware and measured as a function of casting time. The filtration was stopped before the liquid layer reached the top of the cake and the remaining liquid was then removed from the part by pipet. The wet cake volume was determined by mass balance of the system components, including recovered filtrate and excess disperson. The dry cake mass and geometric volume were determined after the parts had been dried at 50°C in an air ventilated oven.

Four point bending was performed on ROCed B_4C/Al test specimens (3 mm X 4 mm X 45 mm). Bend specimen preparation and test procedures were in accordance with the military specification MIL STD 1942.

RESULTS AND DISCUSSION

Powder Characterization

The B_4C powder was supplied as 20-80 μm spherical agglomerates (presumably from spray drying). The particle size distribution by sedimentation was between 0.1 - 3.0 μm (median ~ 1.0 μm). The BET surface area (N_2, 77 K) was 9 m^2/g. Major impurities included 1.3% oxygen, 0.4% nitrogen, and 0.5% residual graphite. The Al powder was a >325 mesh (nominal 4 μm diameter) powder of ~99% purity. Impurities (from neutron and X-ray analyses) included oxygen (0.7%), iron (0.2%), and silicon (0.1%). The BET surface area (Kr, 77 K) was 0.54 m^2/g. No significant increase in the oxygen content of the ceramic or metal powders was detected, even after months in ambient atmosphere.

Dispersion Properties

Because water and alcohols are corrosive to aluminum,[9] toluene was chosen as the fluid medium for dispersion. Other candidate solvents such as aliphatic hydrocarbons and ethers were not evaluated. All of the sedimentation and viscosity results reported here were obtained with ESK 1500 B_4C.

The sedimentation volume of 5 v/o ESK B_4C in toluene is shown in Table 1 for a variety of additives. A loading of 2% additive per dry weight of powder was found to be sufficient to obtain the minimum sedimentation volume for each dispersant. The most effective dispersants were considered to be those which allowed the highest particle packing or lowest sedimentation volume.

Previous study of boron carbide powders has shown the surface to be dominated by the acidic properties of a boric acid overlayer.[11,12] Inspection of Table 1

* Micron Separations, Inc., Distributed by Fisher Scientific, Cat. No. F02-LP090.
** Fisher Scientific, Cat. No. 09-753-25E, 316 SS, 750 mL capacity, 75 mm diameter.

Table 1. Sedimentation Data for ESK 1500 B$_4$C (3.15g in 25 mL toluene).
Additive concentration is 1.5-2.5% vs. dry weight powder.

mg	Dispersant	Sed. Vol. (mL)
63.0	Hypermer KD3 proprietary amine-capped polyester	2.50
126.0	Acryloid B-99 50% PMMA/PBMA copolymer	3.00
78.2	Adogen 471 trimethyl tallow ammonium chloride	3.50
79.5	Alkaterge T oleyloxazoline	3.50
51.6	Emcol CC-36 polypropoxytrialkylammonium chloride	3.50
40.1	Jeffamine D-4000 aminated polypropyleneoxide, 4000 MW	4.00
70.5	Petrosul M60 60% sodium petroleum sulfonate	4.25
44.0	Adogen 349 distearyl methylamine	4.50
60.9	Emphos CS-1361 phosphate ester of ethoxylated alkylphenol	4.50
42.4	Adogen 172-D oleyl amine	4.75
46.2	Jeffamine D-2000 aminated polypropylene oxide, 2000 MW	4.75
38.9	Witcamine PA78B oleyl imidazoline salt	4.75
46.2	Adogen 142-D stearyl amine	5.00
45.3	Adogen 185 3-aminopropyl ether of C$_{12}$-C$_{15}$ alcohol blend	5.00
35.2	Varonic T-205 ethoxylated tallow amine	5.00
33.8	Witcamide 511 diethanol oleylamide	5.00
55.4	Adogen 115-D soya amine	5.25
47.5	Adogen 572 3-aminopropyl oleyl amine	5.75
42.3	Adogen 382 triisodecylamine	6.75
49.3	Adogen 163-D lauryl amine	8.50
43.8	Jeffamine D-400 aminated polypropyleneoxide, 400 MW	11.50
48.8	Kellox Z3 Menhaden fish oil	12.00
34.1	Tergitol NP-4 ethoxylated nonylphenol	13.00
33.9	Pluronic L121 ethoxylated polypropylene oxide, 4400 MW	14.00
44.0	oleic acid	16.25
33.6	Starfol OO oleyl oleate ester	18.50
	none	22.00

indicates that the most effective dispersants had excellent solubility in toluene. The presence of a basic functional group (i.e., amine, oxazoline, and imidazoline groups) which should have strong attraction for the acidic powder surface was beneficial, but of lesser importance. The series of experiments with the Adogen fatty amine additives reveals a gradual decrease in sediment volume with an increase in the number and length of the fatty tail groups bonded to the amine group. Nonionic, ethoxylated surfactants (Tergitol NP-4, Pluronic L121) were not effective, perhaps due to their relatively poor solubility in toluene. The Jeffamine polypropyleneoxide surfactants were more active due to the greater solubility of their polymer chains in toluene and the basic character of the amine capping group. The Emphos CS-1361 and Petrosul M60 dispersants with strongly ionic functional groups and excellent solubility in toluene were also very effective and indicated that functional group polarity may be more critical than acidic or basic character.[13] Additives such as fish oil, oleic acid, and Starfol OO had good solubility in toluene but were not
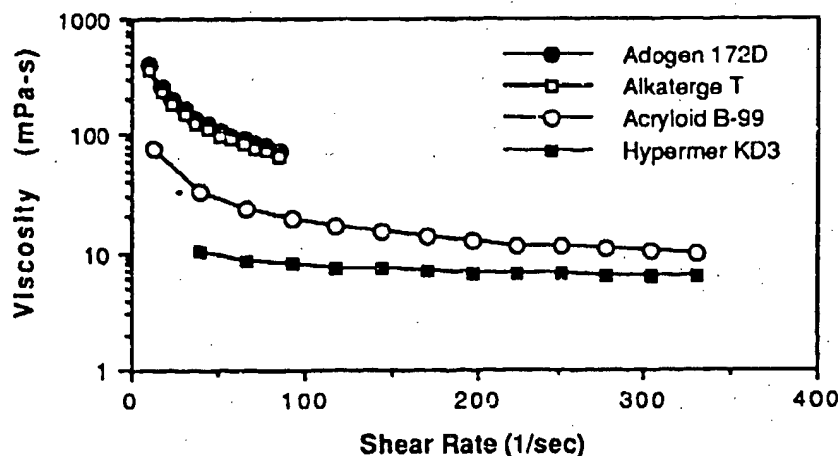
Figure 1. The Viscosity of 70/30 (vol ratio) B_4C/Al Dispersions in Toluene (35 v/o total solids, 2% dispersant vs. dry weight solids).

effective, presumably because of a combination of low molecular weight and low affinity for the acidic B_4C surface.

Three types of sedimentation behavior were observed in the B_4C experiments. (1) In the most stable dispersions a cloudy supernatant persisted throughout the experiment and a dense sediment cake grew slowly from the bottom of the tube. (2) In the least stable dispersions the entire solid mass "slumped" rapidly to its final volume and left a clear supernatant, usually within 1 h. (3) Weakly flocculated particles settled rapidly to yield a clear supernatant and then continued to rearrange and pack into a relatively dense cake. Most of the systems in Table 1, were of the latter weakly flocculated type, which Aksay and co-workers have described as "lubricated" systems.[10] Only the Hypermer KD3 and Acryloid B-99 polymeric dispersants exhibited cloudy, fully stabilized dispersions (type 1).

Sedimentation of the Al powder (3.38 g in 25 mL toluene) was relatively insensitive to the dispersant added, possibly because of the large particle size and low surface area of the powder. Settling was quite rapid and usually complete within 30 min. A sediment volume of 2.00 to 3.00 mL was obtained for dispersions with 2% of the additives Hypermer KD3, Acryloid B-99, Alkaterge T, and Adogen 172D. With no additive the sediment volume was 8.50 mL.

Dispersants for viscosity testing were selected for their sedimentation performance and low ash content (i.e., Na^+ or Cl^-). In accordance with the sedimentation data, the weakly flocculated dispersions containing the short chain surfactants, Adogen 172-D and Alkaterge T, were more viscous and more shear sensitive than the dispersed systems containing the polymeric additives, Acryloid B-99 and Hypermer KD3 (Figure 1).

Table 2. Casting Time and Cake Density for Filter Cast B_4C/Al Greenware (207 kPa (30 psig), 40 v/o solids, 2% dispersant).

Dispersant	Casting Time (min) (for 1.25 cm Cake)	Wet Cake Density (% TD)	Dry Cake Density (% TD)
Adogen 172D	5.6	50	58
Alkaterge T	5.0	52	60
Acryloid B-99	25.0	57	62
Hypermer KD3	33.3	62	62

Casting Properties

Filtration at constant pressure is described by[14]

$$\frac{dt}{dV} = K_p V + B$$

where $\quad K_p = \dfrac{c\,\alpha\,\mu}{P\,A^2} \quad$ and $\quad B = \dfrac{R_m\,\mu}{P\,A}$

and where t is time, V is the filtrate volume, c is the mass of solids deposited per volume of filtrate collected, α is the specific cake resistance, μ is the viscosity of the filtrate, P is the total pressure drop across the filter cake and membrane, A is the cross sectional area of the filter, and R_m is the resistance of the filter membrane. Values for dt/dV were estimated as $\Delta t/\Delta V$ for adjacent points in the volume vs. time
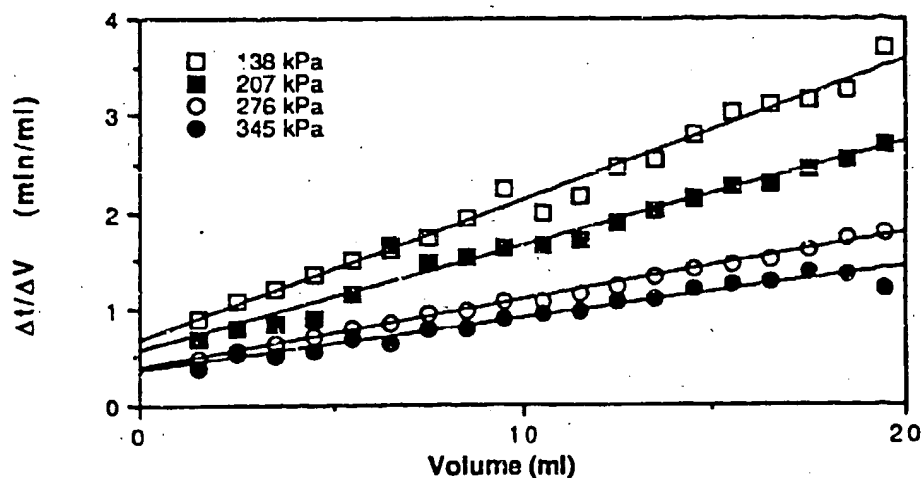
Figure 2. Filtration Rate Plot for 70/30 B_4C/Al in Toluene (2% Hypermer KD3 dispersant).
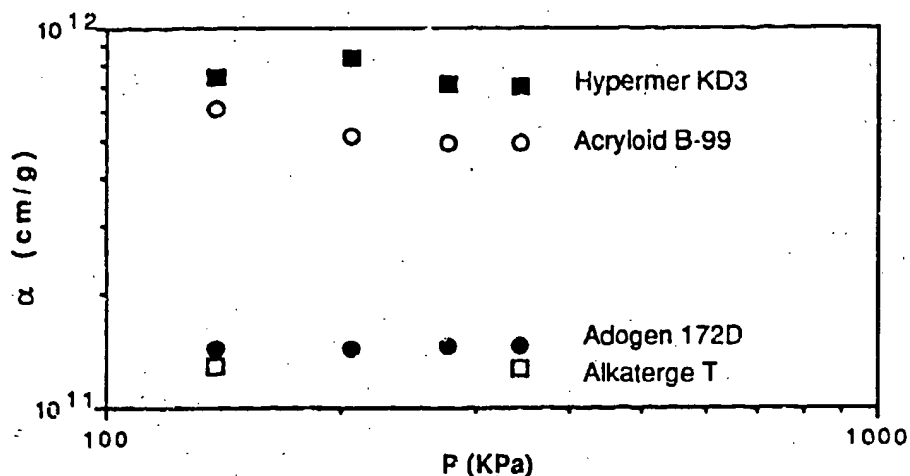
Figure 3. Cake Resistance for Filter Casting Formulations as a Function of Filter
Pressure.

data. The volume V was taken to be the mean of adjacent points. The value of c
was calculated from the final cake mass over the final filtrate volume. The filtrate
viscosity μ was measured relative to that of pure toluene in the ULA spindle of the
Brookfield viscometer.

Formulations with the polymeric dispersants, Hypermer KD3 and Acryloid B-
99, required longer casting time than the Adogen 172D and Alkaterge T formula-
tions, but resulted in higher wet packing density (Table 2). Due to the greater dry-
ing shrinkage of the parts from the Adogen 172D and Alkaterge T formulations, the
final dry cake densities approached those obtained with the polymeric additives.
Filter cake resistance (α) was calculated from the slope of $\Delta t/\Delta V$ vs. V for filtrations
run at different pressures (Fig. 2). For a compressible filter cake, α should in-
crease with increasing pressure. A plot of α vs. P (Fig. 3) gave no indication of
cake compression in any of the formulations between 138-345 kPa (20-50 psig).
The small increase in cake resistance at low pressure for the Hypermer KD3 and
Acryloid B-99 dispersants was likely to be due to sedimentation since the casting
time was fairly long under these conditions. Sedimentation would cause the filter
cake height to increase faster than by filtration alone and, thus, result in a higher
than expected specific cake resistance. As expected from the compressibility data,
the density of the filter cakes was also insensitive to pressure in the range studied.

Dense Cermet Properties

Two cm thick castings of 70/30 B_4C/Al from the Hypermer KD3 and Adogen
172D formulations were heated to 500°C in nitrogen to remove the organic additives
and then densified by Rapid Omnidirectional Compaction (ROC). The density of
the recovered parts ranged from 2.50-2.55 g/cc and indicated residual porosity;

theoretical density depends on the amounts of ternary $Al_xB_yC_z$ phases formed, but is usually ≥ 2.57 g/cc. The cause for this porosity is still under investigation, but is probably due to gas formation during densification or insufficient packing efficiency of the B_4C powder.

Flexural strengths of the densified B_4C/Al from different casting formulations were determined without further heat treatment. Parts cast from with Hypermer KD3 dispersant had a mean flexural strength of 413 MPa ($\sigma = \pm50$ for 13 bars), while the weakly flocculated Adogen 172D dispersant gave 310 MPa ($\sigma = \pm140$ for 17 bars). Although the statistical significance is questionable, the more uniform mixing and particle packing in the parts prepared with Hypermer KD3 dispersant appeared to yield stronger and more reliable material.

CONCLUSIONS

The colloidal stability of the 70:30 (vol%) B_4C/Al powder dispersions in this study was dominated by the boron carbide powder because of its higher surface area than the Al powder. Short chain amine surfactants were generally effective in reducing the sedimentation volume of B_4C in toluene, but still produced flocculated suspension characteristics (rapid settling, clear supernatant). Highly stable dispersions were obtained with the polymeric additives, Hypermer KD3 and Acryloid B-99. Pressure casting of 40 vol% dispersions with 70/30 B_4C/Al slurries has been used to prepare 50-52% dense wet cakes with short chain amine dispersants and 57-62% dense wet cakes with effective polymeric dispersants. Wet cake density was found to be a much more sensitive indicator of dispersion quality than dry cake density. Analysis of volume vs. time data from pressure casting trials indicates that the wet filter cakes are incompressible for filtration pressures between 138-345 kPa (20-50 psig). Dense parts from dispersed casting formulations yielded higher mean flexural strength than those from weakly flocculated formulations.

ACKNOWLEDGEMENTS

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APPENDIX

The following additives were obtained from the manufacturers indicated: Acryloid® B-99 (Rohm & Haas, Philadelphia, PA); Adogen® 115-D, 142-D, 163-D, 172-D, 185, 349, 382, 471, 572, Starfol® OO, Varonic® T-205 (Sherex Chemical, Dublin, OH); Alkaterge® T (Angus Chemical, Northbrook, IL); Emco!® CC-36, Emphos® CS-1361, Witcamide® 511, Witcamine® PA78B (Witco Chemical, Houston, TX); Hypermer® KD3 (ICI Americas, Wilmington, DE); Jeffamine® D-400, D-2000, D-4000 (Texaco Chemical, White Plains, NY); Kellox® Z3 (Spencer Kellog); oleic acid (Fisher Scientific); Petrosul® M60 (Penreco, Butler, PA); Pluronic® L121 (BASF Wyandotte, Parsippany, NJ); Tergitol® NP-4 (Union Carbide, Danbury, CT).

APPENDIX C
THE EFFECT OF B-C-AL PHASES ON MECHANICAL PROPERTIES OF B_4C/AL BASED MATERIALS
Aleksander J. Pyzik and Donald R. Beaman

THE EFFECT OF B-C-AL PHASES ON MECHANICAL PROPERTIES OF B4C/AL BASED MATERIALS

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B_4C/Al cermets were fabricated using the ROC process and then post heat-treated to form multi-phase ceramic materials with a variety of designed compositions. It was found that the major phases influencing the mechanical properties of B_4C/Al based materials were Al_4BC, AlB_2, $AlB_{24}C_4$ and Al_4C_3. Because undesirable Al_4C_3 accompanies the formation of $AlB_{24}C_4$, heat-treatment should be limited to temperatures below 1000°C. At these temperatures, AlB_2 and Al_4BC are the dominant phases. Materials with the majority of the metallic aluminum reacted to form Al_4BC had high hardness and stiffness. Heat-treatment at 600°C and below improved both fracture toughness and flexure strength while heat-treatment above 600°C reduced flexure strength. It was shown that post-densification heat-treatment can be used as a tool to improve some properties of B_4C/Al cermets, as well as to change the two-phase cermet into a multi-phase ceramic containing only a few percent of residual metal.

I. Introduction

Much research work on ceramic containing systems is devoted to studies involving the quality of starting powders, formation of greenware, and densification processes. In contrast, this paper describes boron carbide based materials whose properties can be tailored by *post-densification* heat-treatment analogous to metals. In dense B_4C/Al cermets, the aluminum metal can be largely depleted through the formation of B-C-Al phases with up to 70 volume % of the material consisting of new binary and ternary phases. While the existence of some of these phases has been reported for B-C-Al and B_4C/Al systems [1-4], the exact effect of their presence on mechanical properties is unknown.

The purpose of this work is (i) to characterize low temperature chemistry in the B_4C/Al system, (ii) to develop processing conditions leading to the formation of selected ceramic phases, and (iii) to determine the effect of these "in situ" produced B-C-Al phases on the mechanical properties.

Dense B_4C/Al materials can be achieved using infiltration[5] or, as in this work, through Rapid Omnidirectional Compaction (ROC).[6] ROC is a quasi-isostatic consolidation process in which high isostatic pressure (830 MPa) is applied for a short duration time (5-10 seconds). A powder compact is subjected to pressure delivered through a molten glass or glass-ceramic mixture which is capable of plastic flow. Some benefits provided by ROC are illustrated in the DSC scan shown in Figure 1. The Al melting endotherm at 660°C is followed by a reaction exotherm at about 700°C, a reaction endotherm at about 1010°C, and another endotherm at about 1180°C. ROC processing is done near the melting point of aluminum therein, suppressing the formation of low temperature phases while eliminating the formation of any high temperature phases. Thus, ROC provides *cermets* with limited B-C-Al phases, which can be post heat-treated to form multi-phase *ceramic materials* with a variety of designed compositions, structures and properties. The goal is to broaden the use of B_4C

based material which is presently limited by difficulties in densification by processes other than hot pressing and by the extreme brittleness of B4C.
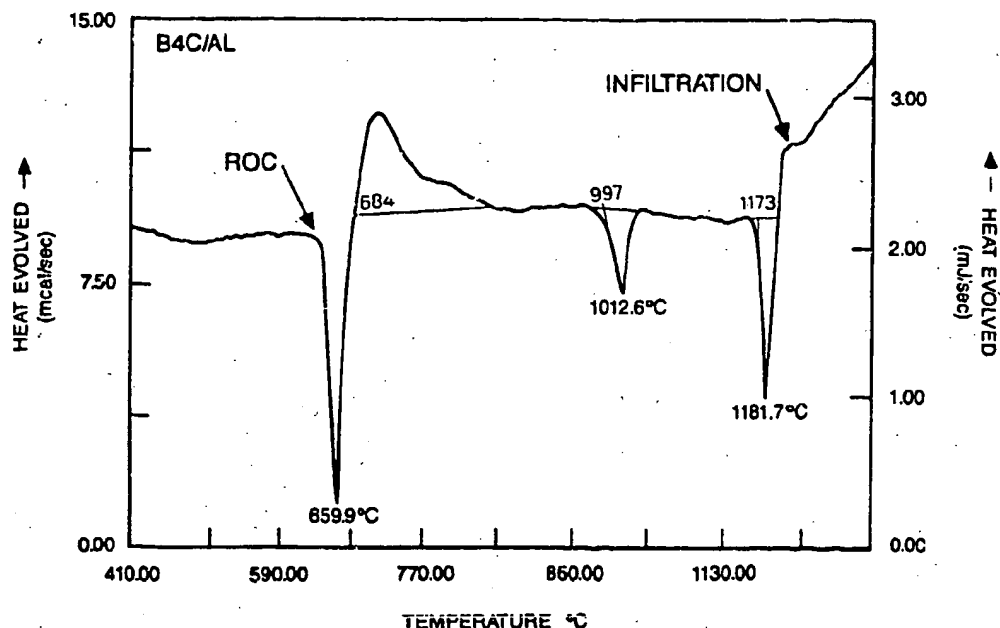

Fig. 1. DSC scan of boron carbide/aluminum powder
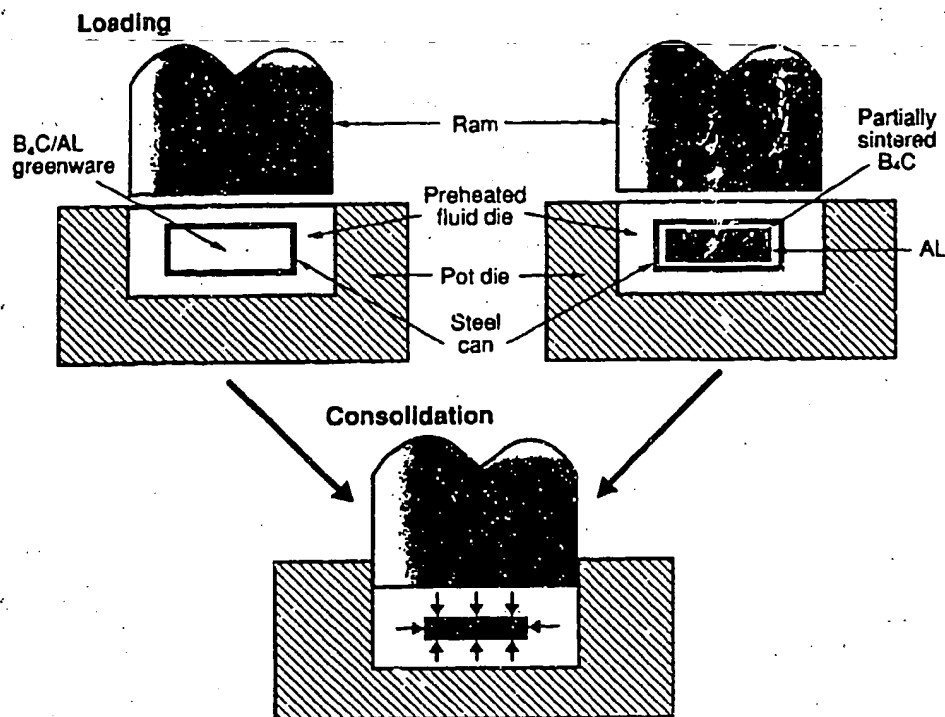
II. Experimental Conditions

(1) Raw materials

The boron carbide used in this study was a Dow developmental powder with 21.27 wt. % total carbon content of 21.27 %, 0.4 % free carbon , 1.27 % oxygen and a surface area of 6.8 m^2/g; the major impurities are 161 ppm Ca, 142 ppm Cr, 268 ppm Fe and 331 ppm Ni. The aluminum powder (Alcan 105) produced by Alcan-Toyo America, Inc. , contained 0.8 % Al_2O_3, 0.18% Fe and 0.12% Si and had a surface area of 0.5 m^2/g.

(2) Densification technique

Two different types of B4C/Al were prepared. In one, the boron carbide and aluminum powders were dry mixed in a rotary blender and then pressed into 75 mm diameter discs using uniaxial compaction in a stainless steel die. No lubricants (binders were used. In the other, 75 mm diameter discs of slip cast B4C that had been sintered to 70% of theoretical density were surrounded by aluminum metal and sealed under vacuum at 550°C in steel cans. The sealed cans were placed in fluid dies. The fluid dies with mixed B4C and Al powders were heated in the furnace to 640°C while the fluid dies with

Loading

B₄C/AL greenware

Ram

Partially sintered B₄C

Preheated fluid die

AL

Pot die

Steel can

Consolidation

Fig. 2. Schematic illustration of the ROC densification technique

samples of partially sintered B4C were heated to about 700°C. Afte· reaching maximum temperature the fluid dies were removed from the furnace, placed in a forging press, and compacted. Schematic illustration of the ROC is presented in the Figure 2. The samples were broken out of the glass die and ground to remove residual glass. The discs were cut into various shapes for testing and characterization.

(3) Heat-treatment procedure

ROCed samples were placed in graphite boat on layer of partially sinter.d boron carbide flakes and covered with thin aluminum foil. Heat-treatmer·t was carried out in a mullite tube furnace under flowing argon. The heating time from 1 oor.1 temperature to the heat-treatment temperature (450 - 1200°C) was 1 hour, while the tin.e at the maximum temperature was 1 to 50 hours, with cooling requiring about 3 hours. In addition to ROCed samples, B4C/Al greenware was heat-treated to determine kinetics of phase formation. Boron carbide and aluminum *powders* were mixed and pressed into 24 mm diameter pellets, heat-treated for one hour in the same furn.·ce, in flowing argon, cooled to room temperature by slow cooling at about 10°/minute. ur quenching into liquid nitrogen.

(4) Characterization

The area of the aluminum melting endotherm in the high temperature DSC scan was used as a measure of the reactivity between B4C and Al at temperatures b·tween 550°C and 1200°C. The data were collected using a Perkin-Elmer DTA 1700 interfaced to a

TADS computer. Ultra high purity argon flowing at about 70 cc/min was used as the purge gas. The samples were heated in alumina crucibles at about 20°C/min. High purity aluminum (99.999%) was used as a standard. The percent aluminum metal was given by A/B x 100, where A is the peak area in cal/g of the Al melt endotherm in the sample and B is the same for the Al standard. Precision and accuracy were about 2 percent.

Crystalline phases were identified by x-ray diffraction with a Philips diffractometer using CuKα radiation and a scan rate of 2° per minute. The chemistry of all phases was determined from electron probe analysis of polished cross-sections using a CAMECA CAMEBAX electron probe. The accuracy in the determination of elemental composition was better than 3% of the amount present.

The broken pieces from 4-point bend testing were used to measure the density in an Autopycnometer 1320 (Micromeritics Corp.) with an accuracy of 0.01 g/cm^3.

Samples for transmission electron microscopy (TEM) were prepared in the following manner: 3 mm diameter x 1 mm thick discs, cut with an ultrasonic disc cutter, were thinned to 100 μm with diamond plates and laps and finished on both sides using 1 μm diamond. Dimpling with 1 μm diamond reduced the thickness to 15 μm and the final thin section was obtained by Ar ion/atom milling from both sides using a liquid nitrogen cooled stage. 5 kV and 2-3 milliampere current.

Bulk hardness was measured on surfaces polished successively with 45, 30, 15, 6 and 1 μm diamond paste and colloidal silica suspension on a LECO automatic polisher. The Rockwell A hardness was measured using a 13.3 kg load. The Vickers microhardness of isolated phases was measured using a LECO tester and loads of 10 to 20 grams. The largest grains of a particular phase were examined in order to eliminate or minimize the contribution from adjacent or underlying material. Generally, the distance from the center of the indent to the nearest grain boundry was over twice the indent diagonal dimension. The indent diagonals were measured in an scanning electron microscope at 10000X.

Fracture toughness was measured using the Chevron notch technique and standard 4 x 3 x 45 mm samples. The notch was produced with 250 μm wide diamond blade and the notch depth to sample height ratio was 0.42. A cross head speed of 0.05 mm/minute was used in a 3 point bend fixture. The average of 5 to 7 measurements is reported. The calculations were made based on equations reported by Shang-Xian[7].

Flexure strength was determined from the average of 8 - 10 measurements on 3 x 4 x 45 mm samples and was performed according to MIL-STD-1942 standard.

III. Results and Discussion

(1) B-C-Al system

Even though at least nine ternary and binary phases have been reported for the B-C-Al system only the four shown in Figure 3 were found to form in significant quantities in this investigation.

Al$_4$BC was first reported by Halverson et al[3] as an unidentified Phase X. In a more recent study, Sarikaya et al[8] found the crystal structure to be hexagonal and the composition to be Al$_4$BC. Wood and Beaman found[9] that the solubility range of
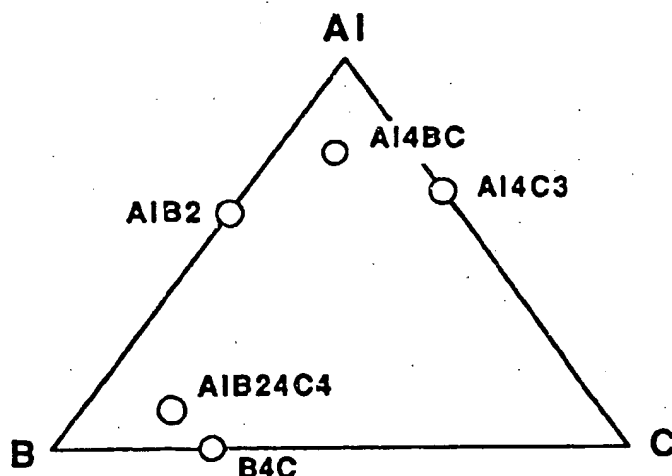
Fig. 3. Major ceramic phases in B4C/Al system (450°C to 1200°C)

aluminum in Al4BC varied from about 69 to 84 percent. Al4BC having typically 83 to 84% of Al is formed during initial stage of reactions, whereas heat-treatment produces Al4BC with only 69 to 76% Al (which corresponds rather to $Al_{2.6}B_{1.8}C$ or $Al_3B_{1.2}C$ than to Al4BC). The composition of this ternary phase lies somewhere between $Al_{2.6}B_{1.8}C$ and Al4BC depending on the processing conditions, and shifts towards lower metal content as chemical reactions proceed. In this report, the phase is discussed as Al4BC, notwithstanding the fact that the exact chemical composition may vary as described.

$AlB_{24}C_4$ and AlB_{10} have been identified as the same phase.[10-12] Will[13] first demonstrated the existence of $AlB_{24}C_4$ as an independent phase. Wood and Beaman[9] confirmed the formation of a phase with the chemical composition of 8% Al, 78% B and 14% C, i.e., the $AlB_{24}C_4$ composition. This this phase formed at 1000°C, well below the 1600°C to 1700°C reported by Will. The crystal structure of this phase does not correspond to high temperature $AlB_{24}C_4$ but rather to $AlB_{12}C_2$, described by Lipp and Röder.[11] Because several assumptions were made in Lipp's work which could result in chemical composition inaccuracy, it is suggested that the phase described as $AlB_{12}C_2$ is actually a low temperature polymorph of $AlB_{24}C_4$.[15] This low temperature $AlB_{24}C_4$ has a rhombohedral structure, whereas the high temperature $AlB_{24}C_4$ is orthorhombic.

AlB_2, the low temperature phase, has a hexagonal structure characterized by layers of metal atoms alternating with layers of boron atoms in a graphite-like structure. It has been found that the AlB_2 structure can accommodate a variety of metal atoms.[9] Experiments with a 7075 aluminum alloy (containing zinc, copper, magnesium and chromium) showed that while Zn formed a solid solution with Al, the Mg and Cr were integrated into the AlB_2 structure. Processing below 700°C gives B4C/Al based materials with AlB_2 containing 12 % of Mg and about 1.5% of Cr. Post heat-treatment at 800°C (for 10 hours) reduces this Mg to 4.5%, while the average Cr content remains at 1.2%. The Cr distribution is nonuniform.

The crystal structure of Al_4C_3 is hexagonal, and it consists of hexagonal layers of aluminum a ons interdispersed with layers of carbon atoms.[16] It has been reported[17] that evapoi ated thin films of aluminum and carbon react above 450°C to form Al_4C_3. In B_4C/Al system, the formation of Al_4C_3 was reported above 660°C[18]; however, the boron carbide used had about 10% of free carbon making the results uncertain. Earlier work[4] indicated a rapid formation of aluminum carbide above 1200°C and negligible formation below 1000°C. The theoretical density of Al_4C_3 is 2.99 g/cm^3.[19] Four-point bend strength and Vickers hardness values have been measured at 150 MPa and 1230 kg/mm^2, respectively.[19]

(2) Phase equilibrium and kinetics of chemical reactions in B_4C/Al system

The reaction between boron carbide and aluminum starts at about 450°C with the formation of Al_4BC, but the reaction rate is slow until 600°C. Typically, at 550 to 600°C, only about 24 percent of metal can be recovered from the starting 30 volume %. This is due to the powder oxidation during mixing and reaction during heating. Above 600°C AlB_2 forms and aluminum is rapidly depleted, as illustrated in Figure 4. The open circles in Figure 4 represent the amount of unreacted Al metal retained in a B_4C/Al powder mixture after heating for one hour at temperatures between 450°C and 1200°C, and cooling to room temperature at about 10°/minute. The initial composition was 70 volume % B_4C and 30 volume % Al. The open boxes indicate the amount of unreacted metal present after quenching in liquid nitrogen. Between 600 and 700°C, AlB_2 and B_4C are the predominant phases. Above 700°C AlB_2 and Al_4BC are both present and as temperature increases the relative amount of Al_4BC increases. Between 900°C and 1000°C, the dominant reaction product is Al_4BC. At about 1000°C, AlB_2 decomposes and generates free aluminum. Heat-treatment above 1000°C produces mainly $AlB_{24}C_4$ and some Al_4C_3. These data suggest two predominant mechanisms of ceramic (B_4C) and metal depletion in B_4C/Al. Phases formed below 1000°C are
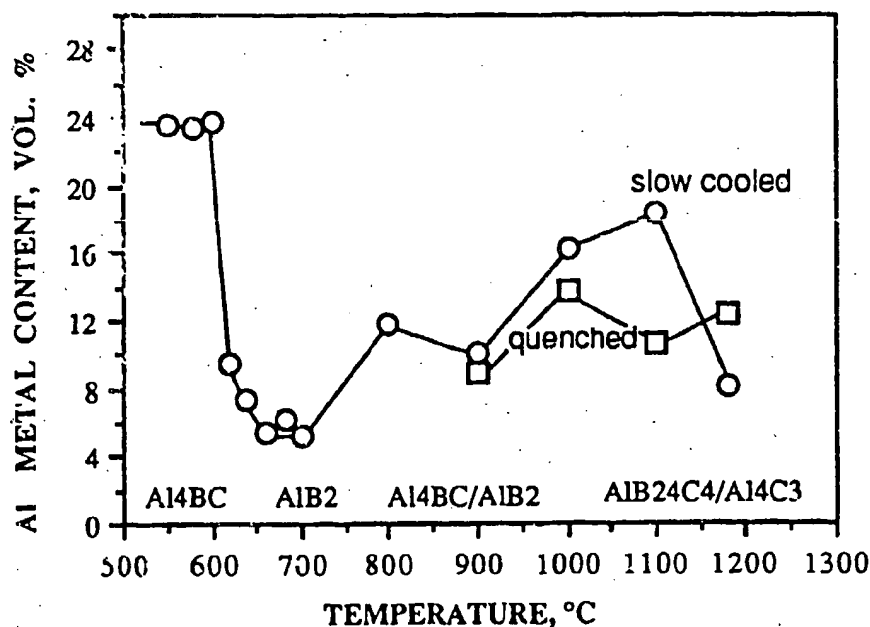

Fig. 4. Phase formation in B_4C/Al system.

rich and their formation leads to the rapid depletion cf metal. Phases formed above 1000°C are boron and carbon rich resulting in B₄C depletion and composites with larger amounts of free metal and smaller amounts of boron carbide than the same starting powders heated below 1000°C.

The cooling rate does not affect the composite composition for temperatures below 900°C, but materials quenched in liquid nitrogen from above 900°C contain less free metal than slowly cooled ones due to the formation of metastable phases above 900°C. During slow cooling, these phases decompose and release additional aluminum.

While the heat-treatment kinetics differ for B₄C/Al powder mixes and previously densified B₄C/Al composites, the same phases are produced. B₄C/30 vol.% Al materials densified by ROCing at temperatures between 640°C and 700°C typically contain 16 to 22 vol.% of unreacted metal. Large ROCed samples (75 mm x 12 mm) undergoing slow cooling, contained 16 3% unreacted metal. In ROCed and heat-treated materials, the amount of Al metal is minimized at 900°C (Figure 5). Heat-treatment above 900°C -1000°C yields aluminum rich cermets. Heat-treatment at 1000°C produces materials with a higher content of aluminum than obtained at lower temperatures, including the solid state reaction at 600°C. This is due to the formation of phases rich in boron and carbon and deplete in aluminum. Figure 5 shows that the reactions proceed faster during first 2-3 hours of heat-treatment. At 600°C and 1000°C, equilibrium is reached after about 20 hours. The initial increase in metal observed at 1000°C is caused by the decomposition of AlB₂. Heat-treatments at 700°C and 900°C require more than 50 hours to reach equilibrium and the depletion of metal beyond 20 hours is slow. The amount of unreacted metal after about 50 hours at 900°C is less than 4 vol.%.
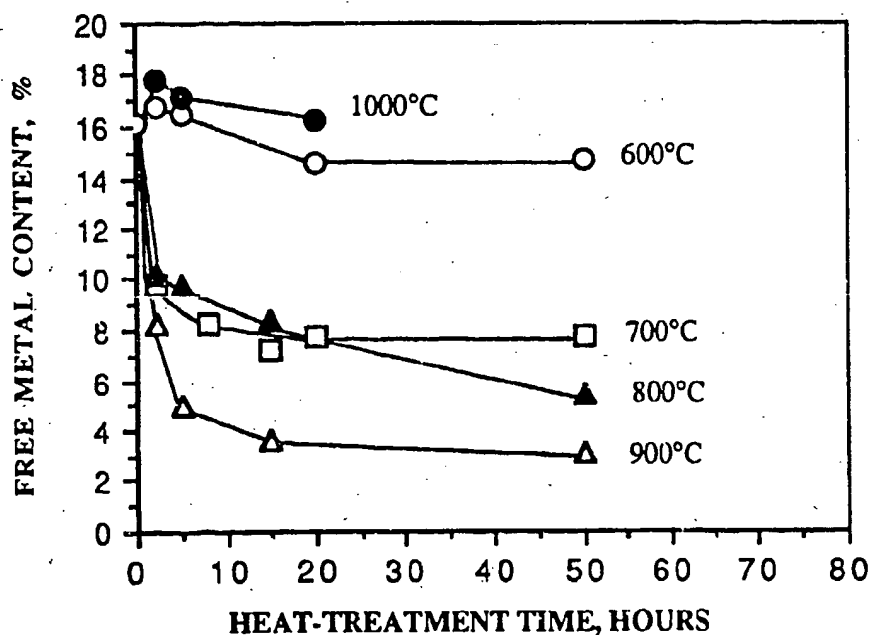

Fig. 5. The kinetics of metal depletion in post heat-treated dense B₄C/Al.

(3) Microstructure

The microstructures of ROCed B$_4$C/Al can range from isolated grains of boron carbide in a continuous aluminum matrix to interpenetrating networks of B$_4$C and metal. Figure 6 shows these two types of materials after heat-treatment at 800°C for 20 hours. Aluminum is mostly depleted. In both cases B$_4$C, AlB$_2$ and Al$_4$BC are predominant phases, however, their spatial distribution, size and connectivity vary.
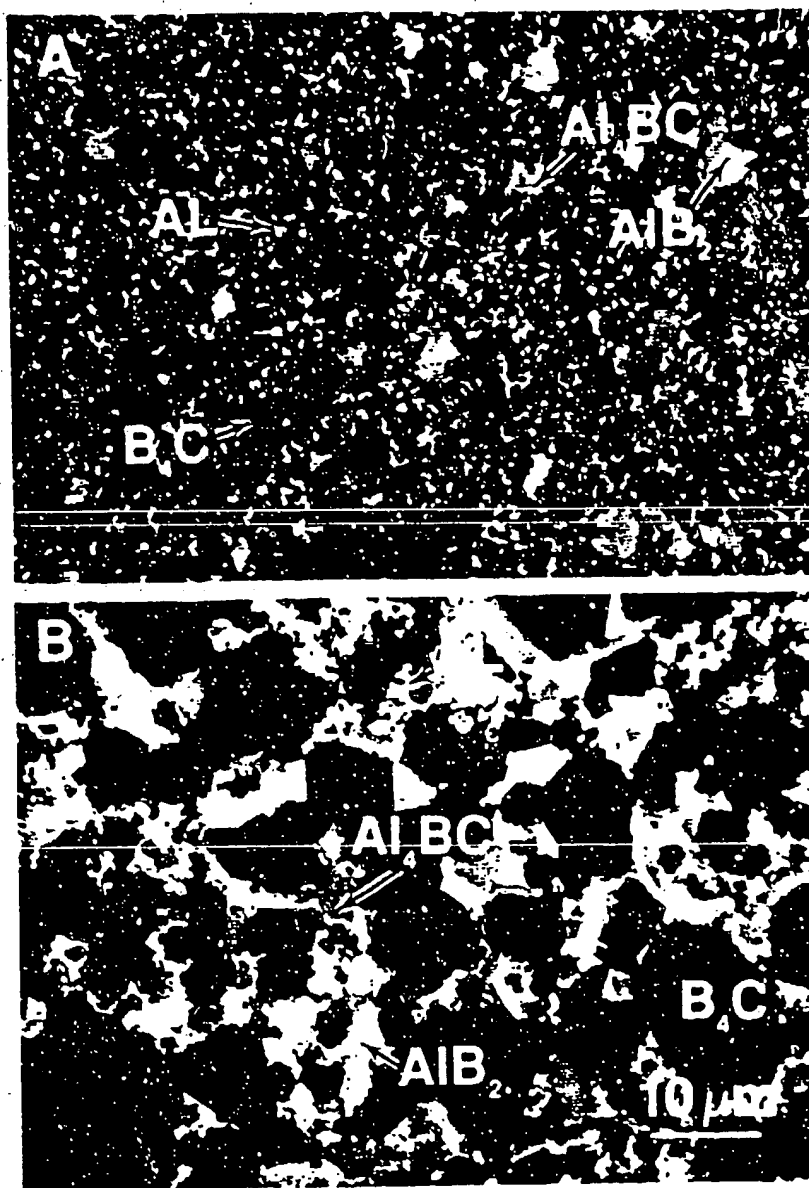
Fig. 6. The microstructures of ROCed 70 vol.% B$_4$C/Al with isolated grains of boron carbide (A) and with interpenetrating networks of B$_4$C and metal (B) after 20 hours heat-treatment at 800°C.

As described above, the phase type and content will depend on the densification temperature and post-heat-treatment time. Table I presents a phase description, useful in microstructural characterization.

Table I. Description of phases in B_4C/Al based system

Phase	Optical microscopy bright field	SEM/ Back scattered electron image	Comments
B_4C	grey	black	usually surrounded by blue-gray Al_4BC
Al	white	white to light grey	
AlB_2	yellow	grey	various shades if contains Cr
Al_4BC	blue-grey; lighter than B_4C	medium to light grey	
$AlB_{24}C_4$	slightly lighter grey than B_4C	slightly lighter colored than B_4C	
Al_4C_3	light grey	light grey	discolors rapidly in air

Metal impurities may result in the formation of additional phases and /or alter the chemistry of aluminum. Copper forms bright crystals of $CuAl_2$. Iron reacts with silicon to form FeSi. Cr and Mg are incorporated into the AlB_2 structure. Zn forms solid a solution with Al but evaporates when heated above 600°C .

(4) The effect of B-C-Al phase equilibrium on the mechanical properties of B_4C/Al based composites

Hardness

The mechanical properties of many B-C-Al phases are unknown with the exception of some microhardness data.[14,15,20,21] The microhardness values measured herein together with literature data, are presented in Table II. The order from hardest phase to least hard is: B_4C and $AlB_{24}C_4$ > Al_4BC > AlB_2 > Al. The Rockwell A hardness as a function of temperature and time are shown in Figure 7. After densification, $B_4C/30$ vol.% Al material has a hardness of about 81. Post-densification heat-treatment at 600°C and 1000°C provides a maximum hardness value of 83 , which remains stable for extended times. At 1000°C, the hardness declines initially due to the decomposition of AlB_2, but then increase again as Al_4BC is formed. Heat-treatments conducted at 700°C, 800°C, 900°C and 1100°C produce a maximum in the hardness versus time curve. The higher the temperature, the less the time required to obtain maximum hardness. This behavior, characteristic of the B_4C/Al system, is again due to the kinetics and B-C-Al phase equilibrium. Below 1000°C, in the initial stage of heat-treatment, hard Al_4BC is favored, but with increased time, there is insufficient aluminum available and softer AlB2 forms decreasing overall hardness. Between 600°C and 1000°C Al_4BC and AlB_2 are both present. Increases in the AlB_2/Al_4BC ratio lower the maximum hardness and
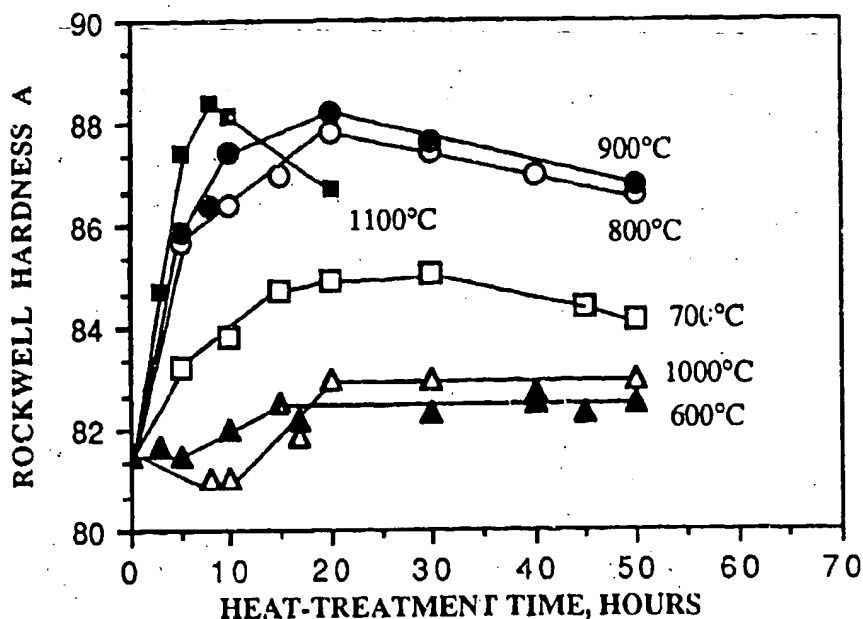
Fig. 7. The effect of temperature and time on the Rockwell A hardness of ROCed and heat-treated B_4C/Al.

make the transition from rising to declining hardness more gradual. After 20 hours of heat-treatment, the AlB_2/Al_4BC ratio is 8, 0.7 and 0.4 at 700, 800 and 900°C respectively. At 1100°C, Al_4BC and then $AlB_{24}C_4$ forms resulting in a high hardness composite. However, after 8 to 10 hours of heat-treatment, Al_4C_3 become the predominant new phase and the hardness declines. The highest hardness values were achieved through heat-treatments of 10 hours at 1100°C (H_{RA} =89), 20 hours at 900°C (H_{RA} = 88) or 20 hours at 800°C (H_{RA}=88).

**Table II.** Hardness of some phases in B-C-Al system.

Phase	Present investigation		Literature data
	2 g load	10 and 20 g load	
B_4C	----	3220	3250-3350[21]
Al	88	125	19[20]
Al_4BC	1310	1400	---
AlB_2	860	1050	980[20]
$AlB_{24}C_4$	3100	----	2530-2650[14]
Al_4C_3	—	1254	1230[19]

Hardness (kg/mm^2)

Flexure strength of B₄C/Al cermets

The flexure strength was measured in B₄C/Al with continuous networks of boron carbide and aluminum and also in samples where the B₄C grains were isolated in a aluminum matrix. Figure 8 shows that the flexure strength of the former microstructure is higher over the entire temperature range, presumably because both phases can carry the load and the boron carbide phase is under higher compressive stress. In addition, the difference in flexure strength may be partially due to the 1 to 2 % density difference between two types of microstructure. Typically, the flexure strength of B₄C/Al decreases with increasing heat-treatment temperature or time at temperature (Figure 8). B₄C/Al with continuous boron carbide have constant strengths from room temperature to 600°C (540 MPa). Between 600 and 800°C, the strength decreases to a minimum of 410 MPa.

In B₄C/Al composites with isolated boron carbide grains, the strength increases slightly for heat-treatment up to 600°C and then decreases sharply to 300-350 MPa.
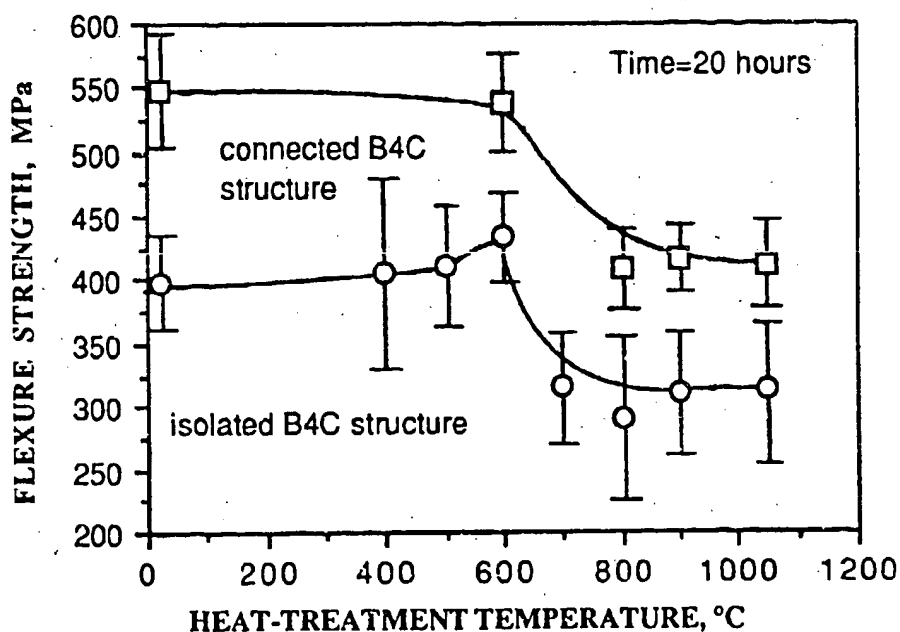
Fig. 8. The effect of heat-treatment temperature on the flexure strength of B₄C/Al composites.

Flexure strength increases from 400 MPa to 435 MPa during the first 20 hours, but then declines (Figure 9) for samples heat-treated at 600°C. This behavior is due to competing mechanisms: metal sintering and the relaxation of ROC induced stresses increases strength during the first 20 hours while the formation of new ceramic phases reduces strength at longer times. For heat-treatments above 600°C, the strength decreases continuously to 300 to 350 MPa regardless of the amount of metal. This decrease is not due to the formation of specific ceramic phases, but rather to phenomena associated with forming new phases in a material, e.g., microcracking.
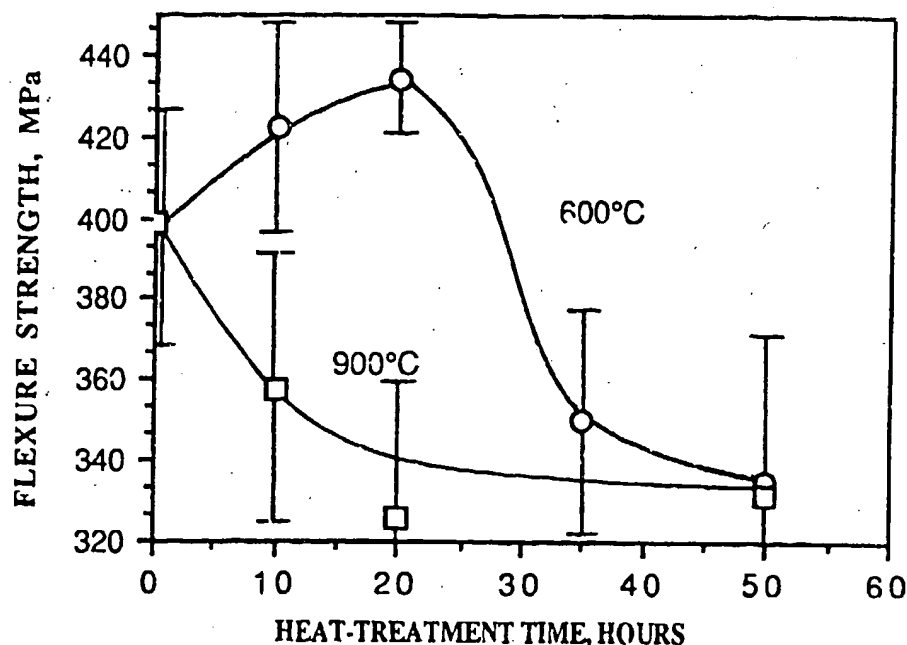
Fig. 9. The effect of heat-treatment time on flexure strength of B4C/Al composites.

Fracture toughness of B4C/Al cermets

The values of the fracture toughness of many B-C-Al phases are unknown. However, the damage and cracking pattern in the indented phases indicates that AlB_2 has a higher toughness than Al_4BC or $AlB_{24}C_4$ (Figure 10). Aluminum containing small ceramic crystals deforms plastically. The damage in AlB_2 represents shear deformation rather than brittle cracking. B_4C and $AlB_{24}C_4$ usually behave similarly, even though, in some cases, the crack propagates through the $AlB_{24}C_4$ and stops at the boron carbide grain boundry (Figure 10 D). Al_4BC shows brittle behavior (Figure 10 C) with several cracks running from the corners and sides of the indent.

Published [22-24] fracture toughness values for B4C/Al range from 6 MPa $m^{1/2}$ to 16 MPa $m^{1/2}$. This variation is due to material differences, including the amount of metal, composition of the Al alloy and metal distribution as well as the shape, size and connectivity of the ceramic phases. In addition, problems are caused by the difficulty in obtaining stable crack growth. In this work, the Chevron notch technique did not produce stable crack propagation in all samples. Low fracture toughness was associated with unstable cracking whereas high toughness was associated with stable cracks. Thus, the true K_{IC} values for the more brittle materials are probably lower than reported.

Fig. 10. Damage observed in the indented crystals of Al (A), AlB$_2$ (B), Al$_4$BC (C), and Al$_4$BC (D).

The results in Figure 11 indicate that post-densification heat-treatment can substantially improve the fracture toughness. The increase is observed only in materials containing isolated grains of boron carbide. In continuous boron carbide structures, K_{IC} decreases slowly as a function of additional heat-treatment. Because B_4C/Al composites with highly continuous boron carbide structure are chemically more stable, after heat-treatment they contain more residual free metal than B_4C/Al composites with isolated ceramic phases.[5] The fact that materials with more ductile phase have lower K_{IC} values indicates that the toughness is controlled mainly through the boron carbide phase. Therefore, optimization of the connectivity in ceramic preform would be more effective in improving the fracture toughness than changing the chemistry of the metal through heat-treatment.

In composites with isolated grains of boron carbide, K_{IC} increases over the entire heat-treatment range when compared to the as-ROCed material. Beyond the maximum at about 600°C, K_{IC} decreases. Analytical transmission electron microscopy did not reveal any differences (e.g. precipitation) between the as-ROCed and heat-treated metal phases.
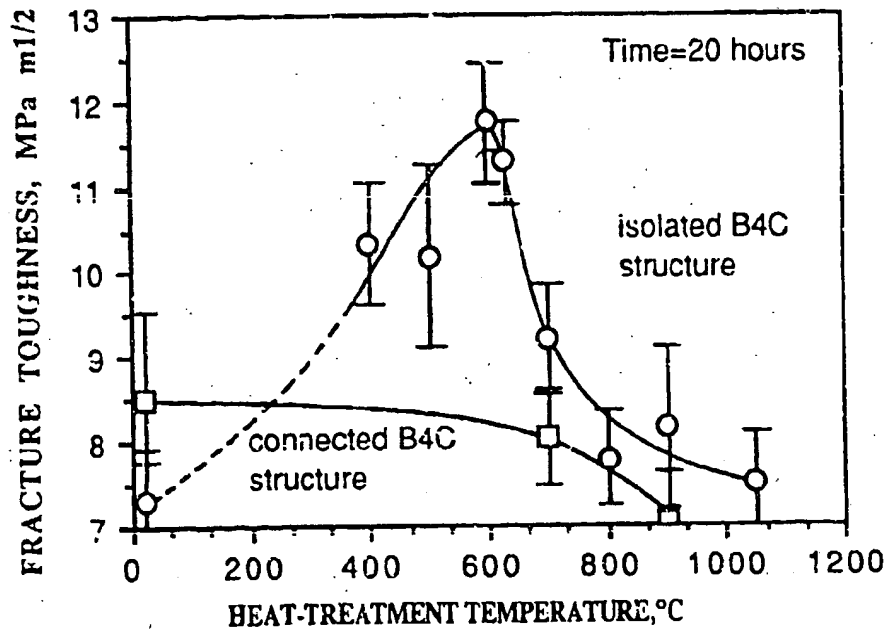

Fig. 11. The effect of heat-treatment temperature on fracture toughness of B_4C/Al composites.

However, a reduction in porosity was observed in the heat-treated samples implying increased density and improved bonding between the ceramic and metal which would account for the increased fracture toughness. At 600°C, where the highest fracture toughness was obtained, sintering of the metal takes place before significant quantities of new phases are formed. The formation of new ceramic phases reduces toughness. The extent of this reduction depends on the type of phases formed. The materials containing AlB_2 have higher K_{IC} values than those with Al_4BC and $AlB_{24}C_4$. It is certainly important to note that all the investigated B_4C/Al materials have at least twice the fracture toughness of pure boron carbide.

IV. Microdesigning Of Material's Properties

It is evident that post-densification heat-treatment can be used to improve many properties of B4C/Al cermets by changing the cermet into a multi-phase ceramic material containing only a small amount of residual metal. Heat-treatment between: 600°C and 700°C produces mainly AlB2; 700°C and 900°C results in a mixture of AlB2 and Al4BC; 900°C and 980°C gives mainly Al4BC; and 1000°C and 1050°C results in AlB24C4 with small amounts of Al4C3 if heating does not exceed five hours.

Table III. The effect of heat-treatment on properties of B4C/Al materials with isolated boron carbide in metal matrix.

Property	After ROC densification	After heat-treatment above 500°C to produce:			After heat-treatment at 600°C
		AlB2	Al4BC	AlB24C4	
Density g/cm³	2.57	2.63	2.70	2.62	2.58
Flexure strength (MPa)	419	357	351	312	434
Fracture toughness (MPa m$^{1/2}$)	7.23	9.21	8.17	7.52	12.7
Young modulus (GPa)	254	290	310	280	260
Bulk modulus (GPa)	138	167	175	156	140
Hardness Rockwell A	81	85	88	88	81
Poisson's ratio	0.23	0.21	0.20	0.20	0.23

From the kinetics at each of these temperatures (see Figure 5), it is possible to produce B4C/Al composites with different phases but similar amounts of residual unreacted aluminum. Table III compares the mechanical properties of as-densified and heat-treated B4C/Al composites. The highest hardness and modulus can be obtained in Al4BC containing samples. While these materials have improved toughness relative to the as densified materials, it is only about 8.17 MPa m$^{1/2}$. On the other hand, AlB2 containing samples exhibit increased fracture toughness (9.21 MPa m$^{1/2}$), but only slight hardness (from 81 to 85) improvement. Because the AlB2/Al4BC ratio can be

changed and controlled by heat-treatment between 700°C and 900°C, the properties of B_4C/Al composites can be selected for a specific application. Processing below $1\text{(} \text{)}°C$ allows the formation of large amounts of AlB_2 and avoids the formation of Al_4C_3.

In heat-treating below 600°C, the new phases form in limited amounts and a multi-phase ceramic is not produced. The resultant B_4C/Al cermets are characterized by a microstructure of isolated boron carbide grains in an aluminum matrix with improved fracture toughness and fracture strength (Table III).

V. Conclusions

1. B_4C/Al cermets represent a category of chemically incompatible materials where post-densification heat-treatment permits tailoring of their chemistry and material properties. Dense, but soft, cermets can be near-net shaped and then changed into hard, ceramic-like material through heat-treatment.

2. The major phases influencing the mechanical properties of B_4C/Al based materials are Al_4BC, AlB_2, $AlB_{24}C_4$ and Al_4C_3. Because the formation of $AlB_{24}C_4$ is associated with the existence of undesirable Al_4C_3, the heat-treatment should be limited to temperatures below 1000°C where AlB_2 and Al_4BC are the dominant new phases.

3. The hardness of B_4C/Al ceramic composites depends upon the kinetics of Al_4BC formation and the AlB_2 to Al_4BC ratio. At temperatures below 1000°C, the maximum hardness of 88 (Rockwell A scale) is achieved after about 20 hours of heat-treatment.

4. The flexure strength of B_4C/Al ceramic composites depends on the continuity of the boron carbide phase. The highest strength was observed when boron carbide and aluminum were both present as continuous phases. A reduction in flexure strength was observed when the heat-treatment was completed above 600°C. It is believed that this reduction is not due to the presence of a specific phase, but rather to phenomena associated with the process of growing new phases e.g., microcracking.

5. An increase in fracture toughness was observed only in materials with isolated grains of boron carbide. This increase was associated with densification of the metal phase. While the formation of ceramic phases reduces toughness, the extent of this reduction depends on the type of phase formed. AlB_2 is the least detrimental.

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KERNFORSCHUNGS JULICH   *DE 3005-586

15.02.80-DE-005586 *(20.08.81)* F41h-05/02

Composite armour plate - using porous, sintered silicon carbide panel which is vacuum impregnated with molten steel

Moulded panel is made of porous SiC with high hardness and high compression strength. The panel is then impregnated with steel, alloy steel, or another metal possessing high- bending and -shear strengths, plus elasticity, after cooling.

USE/ADVANTAGE

Armour plate is produced esp. for military tanks and similar vehicles, which provides protection against hollow explosive charges, but has moderate density.

EXAMPLE

A suspension was made from 100g Si powder; 14g carbon powder; 600 ml ethanol; 6 ml glacial acetic acid; and 61 g phenolic resin binder. The suspension was heated ½ hour at 50°C; cooled; sprayed into 10 l water at 15°C; and the mass obtd. was heated ½ hour at 40°C, then cooled and allowed to settle.

The sludge was filtered and dried to obtain powder, 175g

of which was hot pressed in a die, and then carbonised at 800 °C. in Ar to obtain a panel 10 x 10 x 1 cm, which was heated in Ar to 1600°C.

The panel was next placed in a vessel contg. a bath of Cr-Ni steel at 1600°C. The vessel was evacuated, and the panel was then immersed in the molten steel, followed by using Ar at 20 bars to complete the impregnation. The panel was then taken out of the bath, and cooled.(6pp1144).

DE3005586

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Prüfungsantrag gem. § 44 PatG ist gestellt

㊹ **Panzerung**

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Kernforschungsanlage Jülich
Gesellschaft mit beschränkter Haftung

Für eine Panzerung verwendbare, aus Verbundwerkstoff bestehende Platte,
d a d u r c h   g e k e n n z e i c h n e t, daß die Platte aus einem platten-
förmigen porösen, aus Siliziumkarbid gebildeten Formkörper von hoher Härte
und Druckfestigkeit besteht, der mit Stahl oder einer Stahllegierung oder
einem sonstigen, nach dem Erkalten eine hohe Biege- und Scherfestigkeit
sowie Elastizität aufweisenden Metall oder einer Metallegierung getränkt ist.

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Kernforschungsanlage Jülich
Gesellschaft mit beschränkter Haftung

<u>Panzerung</u>

Die Erfindung bezieht sich auf eine für eine Panzerung verwendbare, aus
Verbundwerkstoff bestehende Platte. Als Werkstoff für Panzerplatten sind
bisher im allgemeinen Stahl oder Stahllegierungen verwendet worden. Diese
Panzerplatten weisen zwar eine hohe Biege-, Scher- und Druckfestigkeit
auf. Doch haben diese Platten den Nachteil, daß ihre Herstellung aufwendig,
ihr spezifisches Gewicht hoch ist und daß sie selbst bei einer solchen Dicke,
wie sie für Panzerplatten von Panzerfahrzeugen noch als tragbar angesehen
werden können, keine hinreichende Sicherheit gegen Hohlladungen bieten.

Aufgabe der Erfindung ist es, eine für Panzerungen, insbesondere für Panzer-
fahrzeuge geeignete Platte zu schaffen, die bei hinreichender Biege-, Scher-
und Druckfestigkeit auch Schutz gegen Hohlladungen gewährleistet.

Diese Aufgabe wird gemäß der Erfindung dadurch gelöst, daß die Platte aus
einem plattenförmigen porösen, aus Siliziumkarbid gebildeten Formkörper
von hoher Härte und Druckfestigkeit besteht, der mit Stahl oder einer Stahl-
legierung oder einem sonstigen, nach dem Erkalten eine hohe Biege-, Scher-
und Druckfestigkeit sowie Elastizität aufweisenden Metall oder einer Metall-
legierung getränkt bzw. imprägniert ist.

Eine solche Platte wird nach einem nicht vorveröffentlichten Vorschlag
unter Verwendung einer pulverförmigen oder körnigen Mischung aus Silizium
und Kohlenstoff und gegebenenfalls unter Beimischung von Siliziumkarbid
hergestellt. Dabei werden die Körner oder Partikeln des Pulvers mit einem
organischen Bindemittel umhüllt. Aus der auf diese Weise gebildeten Masse
wird zunächst durch Plastifizieren des verwendeten Bindemittels ein Grün-

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körper geformt, der im Anschluß daran verkokt wird. In einer weiteren
Verfahrensstufe wird der Formkörper zur Umsetzung des verwendeten
Ausgangsmaterials zu Siliziumkarbid in einer Inertgasatmosphäre unter
einem Druck von etwa 1 bar und höher, um das Abdampfen von Silizium
zu verhindern, auf eine zwischen etwa 1400°C und 1600°C liegende
Temperatur mit hoher Geschwinigigkeit aufgeheizt.

Dabei besteht eine besonders vorteilhafte Ausgestaltung des Verfahrens
zur Herstellung von Panzerplatten gemäß der Erfindung darin, daß zur
Bildung der mit dem Bindemittel überzogenen Körner oder Partikeln
eine Bindemittellösung gebildet wird, in der die Körner oder Partikeln
aufgeschlämmt werden. Im Anschluß daran wird die Aufschlämmung
mittels einer Düse in eine zur Abscheidung des Bindemittels dienende
Flüssigkeit so eingegeben, daß die Körner oder Partikeln mit dem Binde-
mittel gleichmäßig überzogen werden. In einer sich daran anschließenden
Verfahrensstufe wird die Masse der mit dem in dieser Weise mit dem
Bindemittelfilm überzogenen Körner oder Partikeln durch Filtrieren
oder Dekantieren von der Abscheidungsflüssigkeit abgetrennt und ge-
trocknet. Die weiteren Maßnahmen laufen im Anschluß daran in der
zuvor angegebenen Weise ab. (Vgl. auch DT-PS 20 40 252, DT-PS 21 33 044
und DT-PS 23 60 982)

Die dem jeweiligen Verwendungszweck entsprechende genaue Form-
gebung erfolgt bei diesem Verfahren durch Extrudieren oder in einer
Gesenkpresse, wobei lediglich geringe Drucke angewendet werden
müssen. Um eine Vergrößerung der Siliziumkarbidkristallite und infolge-
dessen eine Erhöhung der Verfestigung des Gefüges sowie eine Ver-
größerung der Poren des gebildeten plattenförmigen Siliziumkarbid-
körpers zu erreichen, wird der so vorbehandelte Körper bei Temperaturen
zwischen 1700°C und 2100°C getempert. In einem weiteren Verfahrens-
schritt wird der poröse plattenförmige Siliziumkarbidkörper in einem

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Druckbehälter zunächst evakuiert und sodann in das zum Tränken oder Imprägnieren vorgesehene Metallbad getaucht, wobei ein Druck von bis zu 50 bar ausgeübt wird. Anschließend wird die mit der metallischen Flüssigkeit getränkte oder imprägnierte Platte aus dem Metallbad herausgenommen und nach Abfließen des noch an den Oberfläche der Platte haftenden Metalls langsam abgekühlt. Falls erforderlich, wird an der Oberfläche der Platte etwa noch anhaftendes Metall durch Abätzen entfernt.

Ausführungsbeispiel

Es wurden 100 g Siliziumpulver (Korngröße 270 mesh) und 14 g eines Kohlenstoffpulvers bestehend aus 90 Gew.-% Elektrographit und 10 Gew.-% Holzkohle (Hauptkorngröße 10 μm - 20 μm) in einer Lösung von 600 ml Äthanol und 6 ml Eisessig sowie 61 g Phenolformaldehydharzbinder aufgeschlämmt. Die Aufschlämmung wurde unter Rühren auf 90 ^{o}C erwärmt und nach einer halben Stunde auf Raumtemperatur abgekühlt. Die Aufschlämmung wurde dann durch eine Düse in einen Wasserstrom von 15°C eingespritzt, wobei 10 l Wasser verbraucht wurden. Die gebildete Masse wurde unter Rühren auf 40°C erwärmt und nach einer halben Stunde auf Raumtemperatur abgekühlt. Nach Absetzen des gebildeten Schlammes wurde die Flüssigkeit dekantiert und der Schlamm abfiltriert und getrocknet.

175 g des so gebildeten Pulvers wurden in einen quadratischen Formkasten von 10,8 cm Kantenlänge gleichmäßig eingestreut und mit einem Stempel in einer Presse warmgepreßt. Nach dem Erkalten wurde die gebildete Platte von 10,8 cm Kantenlänge und 1,1 cm Dicke entformt und unter einem Argonstrom durch Aufheizen auf 800°C verkokt. Die Dimensionen der Platte be-

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trugen nach dem Verkoken 10,0 cm Kantenlänge und 1,0 cm Dicke. An-
schließend wurde die Platte in einen evakuierbaren Ofenraum gebracht,
evakuiert und mit Argon geflutet. Unter einem Argondruck von 1 bar wurde
die Platte auf 1350°C aufgeheizt und 5 Minuten auf dieser Temperatur be-
lassen. Danach wurde mit einer hohen Aufheizgeschwindigkeit auf 1600°C
erhitzt und anschließend abgekühlt. Die silizierte Platte wurde sodann in
einen Vakuumdruckbehälter eingebracht, in dem sich ein Bad aus Chromnickel-
stahl auf einer Temperatur von 1600°C befand. Der Vakuumbehälter wurde
zunächst evakuiert, anschließend die Platte in das Stahlbad vollständig einge-
taucht und der Vakuumdruckbehälter mit einem Argondruck von 20 bar beauf-
schlagt. Hierauf wurde die Platte aus dem Bad gezogen und nach dem Ablaufen
des überschüssigen Stahls und langsamem Abkühlen auf Raumtemperatur aus
dem Vakuumdruckbehälter entnommen.

power density electric motor armatures can be made by nitriding both phases simultaneously (Ref 5).

Reaction-Bonded Silicon Carbide

Reaction-bonded silicon carbide represents the most important example of the processes based on reactions between a porous solid and an infiltrating liquid phase. These processes share the near-net shape and near-net dimension capabilities of gas-phase reaction bonding, as well as the reduced processing temperatures relative to solid-state sintering. Also, they may have significant advantages in the processing rates and material densities that are achievable.

Reaction-bonded silicon carbide was first developed in the 1950's by the United Kingdom Atomic Energy Authority (UKAEA, Springfield) as a means of bonding silicon carbide grain into a refractory body. A class of fibrous silicon/silicon-carbide composites was later developed by General Electric Company using carbon fiber preforms. Other carbides have also been synthesized by the liquid metal infiltration of carbonaceous preforms and, in principal, compounds such as borides can be synthesized as well, although much less work has been done in the area. Recently, boride-carbide-metal composites based on reactions between molten zirconium, titanium, and hafnium have been reported (NX-3400).

Conventionally, RBSC material is made by infiltrating a porous carbon shape with liquid silicon and then allowing the two elements to react to form silicon carbide at temperatures somewhat above the melting point of silicon (≈ 1410 °C, or ≈ 2570 °F). This compares very favorably with hot pressing that is carried out at temperatures in excess of 1800 °C (3270 °F) and sintering at $T \geq 2000$ °C ($T \geq 3630$ °F). Generally, infiltration and reaction processes occur simultaneously and involve kinetics that are extremely complex in detail. The process can be extremely fast, due to:

- Rapid infiltration kinetics that result from good wetting of carbon by liquid silicon and low silicon melt viscosities
- Rapid reaction kinetics aided by a large exothermic heat of reaction

In fact, processing problems such as thermal stress cracking more often arise from too fast a reaction rate rather than too slow a reaction rate, as is also the case in SHS processes.

Controlling the residual phase content is a particularly important issue for RBSC material because silicon carbide exists essentially as a line compound (compound having negligible range of stoichiometry) so that either excess carbon or silicon will appear in the fired part. Free silicon is particularly troublesome because the molten silicon expands upon freezing, frequently cracking the part. The kinetics of simultaneous reaction and infiltra-

tion are of particular concern when fine-scale microstructures and low free-silicon fractions are desired, because these kinetics determine practical issues such as the ultimate processable dimensions, the processing rates, and the spatial uniformity of resulting materials. When alloyed-melts are used, there is an additional level of control over the reaction rate as well as the second-phase content. For example, boron additives enhance the silicon-carbide reaction rate, molybdenum has a negligible effect, and aluminum inhibits the rate.

The mechanical properties achievable in RBSC material are a function of microstructure and phase content. Commercially available materials vary in room-temperature flexural strengths from 200 to 600 MPa (30 to 85 ksi), whereas a laboratory material prepared by Hucke (using microporous carbon preforms derived from organic precursors to obtain finer-grained microstructures) has demonstrated strengths up to ≈ 700 MPa (≈ 100 ksi). At high temperatures, the principal deficiency is a marked degradation in strength and creep resistance upon exceeding the melting point of the residual silicon (≈ 1410 °C, or ≈ 2570 °F). Furthermore, a high free-silicon content can be detrimental to mechanical properties; failure flaws apparently initiate at and propagate along the weak silicon/silicon-carbide interface at low temperatures. At elevated temperatures near the melting point of silicon (1200 °C < T < 1410 °C, or 2190 °F < T < 2570 °F), the silicon phase is ductile and has mixed effects. While the presence of the ductile phase can improve fracture toughness and strength by modest amounts, it can also be the initiation source for cavities that lead to creep rupture at long elapsed times.

An approach for eliminating the residual silicon phase that substitutes alloyed silicon infiltrants for pure silicon has recently been investigated at Massachusetts Institute of Technology. The alloying constituent(s) are selected on the basis of their ability to form refractory silicides that are stable with respect to silicon carbide at high temperatures. Upon reactive formation of silicon carbide, the solutes are rejected into the remaining melt, enriching it until the refractory silicide forms. Using the silicon-molybdenum melt system as a model, the reaction is:

$$(x + 2y)Si + yMo + xC \leftrightarrow xSiC + yMoSi_2$$

(Eq 2)
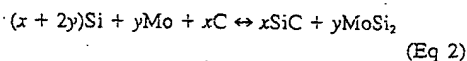
This approach demonstrates that materials free of residual silicon phase that retain the important processing advantages of liquid-phase reaction bonding are possible.

With respect to the processing of fiber-reinforced composites, it is worth noting that the introduction of an inert particulate phase into preforms has been widely used since the initial development of RBSC material. Substitution of fibers and whiskers for the particulate phase should present no particular difficulties except perhaps in the preparation

of preforms. The major issue of concern is the high reactivity of the liquid phase and the severe thermal transients that accompany infiltration and reaction. These are likely to present problems in the control of matrix-fiber interfacial properties. Fitzer and Gadow have prepared a variety of silicon carbide and carbon fiber-reinforced RBSC composites and obtained the best results (inelastic deformation with peak flexural strengths in excess of 300 MPa (45 ksi) and strains to failure in excess of 0.3%) for carbon fiber composites when the pore volume is too low for significant attack of the fibers by the infiltrating silicon melt. The development of appropriate fiber coatings is thus another obvious future direction for these composites.

A recent development in liquid-solid reaction bonding is a class of multiphase composites consisting of a carbide, a boride, and a residual metal that is processed by the reaction between B_4C and a molten metal. For the zirconium system, the reaction is:

$$(2.2 + x)Zr + 0.6B_4C \rightarrow ZrB_2 + ZrC_{0.6} + xZr$$

(Eq 3)
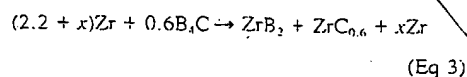
The reaction of Eq 3 is necessarily carried out at temperatures 1850 to 2000 °C (3330 to 3600 °F) above the melting point of zirconium. This is again an exothermic reaction, with processing times on the order of 1 to 2 h. The resulting cermet microstructure contains hexagonal platelets of the diboride in a matrix of the carbide and metal; the residual metal distribution is either discrete or interconnected depending on its volume fraction. The reported properties of this material are excellent and include values for room-temperature flexural strengths of 800 to 900 MPa (120 to 170 ksi) and fracture toughness of 16 to 18 MPa $\sqrt{m}$ (15 to 16 ksi $\sqrt{in}$.).

Additional Reaction-Bonding Processes

Chemical vapor infiltration represents one of the most promising, yet intrinsically difficult, reaction forming processes for making ceramic matrix composites. CVI processes are used to chemically vapor deposit the matrix phase(s) within a porous preform, typically made from the reinforcing fiber phase. Conventional CVI processes were first applied successfully in Europe by researchers at Société Européenne de Propulsion (SEP), Laboratoire de Chimie du Solide du CNRS (French Atomic Energy Commission), and the Institut für Chemische Technik der Universität Karlsruhe, primarily in composites with silicon carbide fibers and matrices. Recent advancements have made important progress with respect to long-standing obstacles.

The potential advantages of the CVI process include:

- Good throwing power (achieving uniform coverage)
- Ability to manipulate the stoichiometry,